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THE COMPOSITION AND INSTABILITY CONSTANTS OF SOME COORDINATION COMPOUNDS OF SILVER

M. B. Shchigol

Our previous reports [1-4] showed that the potentiometric titration of chlorides, iodates, bromates, oxalates and other salts in the presence of ammonia yields various coordination compounds with apparently different coordination numbers for silver (6, 4, 2). Thus, there are two saltuses on the titration curve (Fig. 1) when determining salts of monovalent anions. The first saltus occurs after half the silver nitrate has been added to the ammoniacal solution of the salt (if 5 ml of a 0.1 N solution of the salt were used, the first saltus would appear when 2.5 ml of 0.1 N $AgNO_3$ is added); the second saltus would appear on the curve after all the silver nitrate used in the reaction had been added (i.e., 5 ml of 0.1 N $AgNO_3$). Evidently, the first saltus represents the compound $[Ag(NH_3)_2X_2]^-$ (X representing a monovalent anion) with the coordination number 4 for silver, while the second saltus represents $[Ag(NH_3)_2]^+$ with the coordination number 2 for silver. When salts of divalent anions are titrated potentiometrically, there are three saltuses on the titration curve, the first apparently representing the complex ion $[Ag(NH_3)_2X_2]^{3-}$ with the coordination number 6 for silver (X being a divalent anion), the second representing $[Ag(NH_3)_2X]^-$ with the coordination number 4, and the third representing the complex ion $[Ag(NH_3)_2]^+$ with the silver coordination number 4.

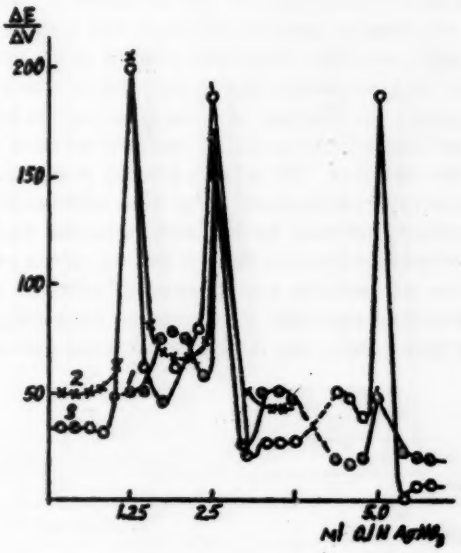

Fig. 1
1 - Titration of 5 ml of 0.1N NaCl solution in 10 ml of 1N ammonia solution; 2 - titration of 2.5 ml of 0.1 N KIO_3 solution in 10 ml of 0.1 N NH_3 solution; 3 - titration of 5 ml of K_2CrO_4 solution in 20 ml of 0.1N NH_3 solution.

The concentration of the complex ion diminishes as the ammonia concentration drops, for a constant salt concentration, the potential of the silver electrode increasing noticeably and the maximum rising at the points of equivalent saturation.

The latter circumstance proves that the ammonia and the salt anion are part of the inner sphere of the newly formed coordination compound, their proportions being identical, evidently. Studying the composition of these compounds is of distinct theoretical as well as practical interest by way of underpinning the previously developed method involving the potentiometric titration of various anions in ammonia.

As we know, there are various chemical and physicochemical methods used in studying the composition and the properties of coordination compounds. The most widely used of these methods are the potentiometric, polarographic, and optical methods. The work of various authors [5, 6, 7] has shown that optical research methods, particularly colorimetry, are wholly satisfactory in studying solutions of colored coordination compounds. The potentiometric and polarographic methods are best suited for research on uncolored coordination compounds. We have employed the potentiometric method for our ternary systems, comprising silver, ammonia, and salt ions.

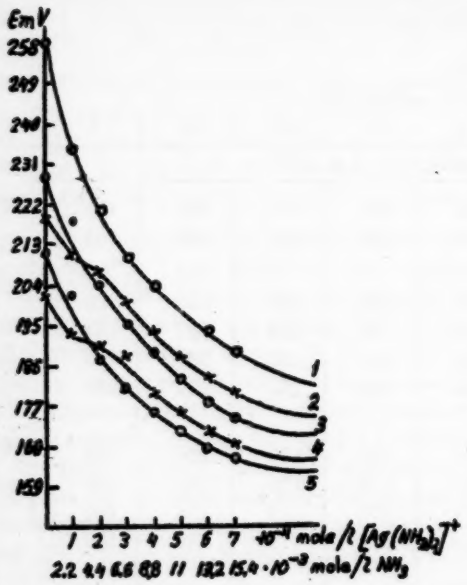

Fig. 4

Change of potentials in a complex system when the salt concentration is held constant and the concentration of ammonia in the solution is varied. Titration with an $AgNO_3$ solution: of water (Curve 1), of 10^{-1} mole/liter BrO_3^- (Curve 2), of $2.5 \cdot 10^{-1}$ mole/liter BrO_3^- (Curve 3), of 10^{-1} mole/liter IO_3^- (Curve 4), and of $2.5 \cdot 10^{-1}$ mole/liter IO_3^- (Curve 5).

where C_{Ag^+} is the concentration of silver ions (in gram-ions per liter); $C_{compl.}$ is the concentration of complex ions (in moles per liter); and C_X is the anion concentration, equalling the total salt concentration.

When the salt and ammonia concentrations are kept constant and the concentration of silver is varied, the ratio

$$\frac{C_{Ag^+}}{C_{compl.}}$$

will be a constant. Hence, the instability constant will depend upon the ratio between the concentration of silver ions and that of the complex ions, rather than upon their absolute values.

Rearranging Equation (2), we get

$$\frac{C_{compl.}\, K}{C_{Ag^+}} = (C_{NH_3} C_{X^-})^z. \qquad (3)$$

By comparing the value of the $C_{compl.}$ ratio at a given salt concentration and at various concentrations of ammonia and silver nitrate (A), we can readily find the value of the exponent z, i.e., the number of coordinated groups (Table 3). The concentration of free silver ions is found from the decrease in the potential of the silver electrode (Tables 1 and 2), as given by the formula:

$$E = E_0 - \frac{0.059}{n} \log \frac{A}{C_{Ag^+}}.$$

Thus, the mean value of z is nearly 2. We must take $[Ag(NH_3)_2X_2]^-$, as the formula for the complex anion, where X is a monovalent anion. Knowing

TABLE 3

	C_{salt}, moles per liter	C_{NH_3}, moles per liter	$C_{compl.}$, moles per liter	C_{Ag^+}, gram-ions per liter	$\log \frac{C_{compl.}}{C_{Ag^+}}$	$z \log (NH_3 \cdot X)$	z
Cl^-	10^{-2}	10^{-1}	$5.5 \cdot 10^{-4}$	$2.7 \cdot 10^{-9}$	5.30	−3.00	
	10^{-2}	$2 \cdot 10^{-1}$	$5 \cdot 10^{-4}$	$7.7 \cdot 10^{-9}$	5.813	−2.70	1.71
	$4 \cdot 10^{-2}$	$4 \cdot 10^{-1}$	$100 \cdot 10^{-4}$	$5 \cdot 10^{-9}$	6.3	−1.80	
	$5 \cdot 10^{-2}$	10^{-1}	$7.7 \cdot 10^{-4}$	$3.44 \cdot 10^{-9}$	5.34	−2.30	1.92
BrO_3^-	$0.567 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2.8 \cdot 10^{-3}$	$5.6 \cdot 10^{-7}$	3.70	−3.947	
	$0.567 \cdot 10^{-2}$	10^{-2}	$7.7 \cdot 10^{-4}$	$5.7 \cdot 10^{-7}$	3.13	−4.25	1.9
	10^{-1}	$0.44 \cdot 10^{-2}$	$2 \cdot 10^{-4}$	$7.3 \cdot 10^{-7}$	2.4	−3.36	
	10^{-1}	$0.88 \cdot 10^{-2}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-7}$	3.00	−3.06	2.00
IO_3^-	10^{-1}	$0.44 \cdot 10^{-2}$	$2 \cdot 10^{-4}$	$7.3 \cdot 10^{-7}$	2.4	−3.36	
	10^{-1}	$0.88 \cdot 10^{-2}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-7}$	3.00	−3.36	2.00
	$5 \cdot 10^{-3}$	10^{-2}	$7 \cdot 10^{-4}$	$5 \cdot 10^{-7}$	3.146	−4.30	
	$5 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$2.5 \cdot 10^{-4}$	$4.6 \cdot 10^{-7}$	3.736	−4.00	1.96

the value of z we can calculate the instability constant of the complex ion. Let the general formula for the complex ion be $[BX_2]^-$, where $B^+ = [AG(NH_3)_2]^+$; then $[BX_2]^- \rightleftharpoons BX + X^-$ and

$$K = \frac{[BX][X^-]}{[BX_2^-]} . \quad (4)$$

Further dissociation of $BX \rightleftharpoons B^+ + X^-$, results in

$$K_{BX} = \frac{[B^+]^2}{[BX]} ; \quad [BX] = \frac{[B^+]^2}{K_{BX}} . \quad (5)$$

Inserting the value for [BX] in Equation (4), we get:

$$K = \frac{[B^+]^2 [X^-]}{A - B} . \quad (6)$$

The concentration "B^+" is calculated from the potential drop in the system. Taking the potential measured when titrating 100 ml of a 0.01N ammonia solution (for IO_3^- and BrO_3^- ions) or 100 ml of a 0.1N ammonia solution (for Cl^- ions) with silver nitrate as E_0:

$$E = E_0 - \frac{0.059}{n} \lg \frac{A}{B^+} .$$

The calculation of the instability constants is given in Tables 4, 5 and 6.

Thus, the mean value of the instability constant for complex ions, of the $[Ag(NH_3)_2X_2]^-$ type, where X is a monovalent anion, is $3 \cdot 10^{-8}$.

TABLE 4 Calculation of the Instability Constants for Complex $[Ag(NH_3)_2Cl_2]^-$

$C_{Cl^-} \cdot 10^2$ moles/liter	$C_{NH_3} \cdot 10$ moles/liter	E, V S. C. E.	E_0, V S. C. E.	$E_0 - E$, V S. C. E.	$C_{Ag^+} \cdot 10^5$ gram-ions/liter	$B^+ \cdot 10^4$ gram-ions/liter	$A \cdot 10^4$ moles/liter	$K \cdot 10^5$
1.0	1.0	0.063	0.377	0.314	2.63	3.47	5.5	0.8
5.0	1.0	0.060	0.377	0.317	2.34	3.00	5.5	1.8
7.5	1.0	0.050	0.377	0.322	1.90	2.50	5.5	1.87
1.0	1.0	0.071	0.383	0.312	3.86	4.40	7.7	0.52
5.0	1.0	0.067	0.383	0.316	3.44	3.85	7.7	1.92
7.5	1.0	0.060	0.383	0.323	2.60	2.90	7.7	1.31
1.0	2.0	0.085	0.428	0.343	7.70	25.00	50.00	2.50
5.7	3.0	0.064	0.428	0.364	7.0	20.00	100.00	2.85
							$K = 1.7 \cdot 10^{-5}$	

Relationship of the $[AgX_2]^-$ Constant to the Constant of the $[Ag(NH_3)_2X_2]^-$ Ion

As we know [8, 9], silver halides dissolve in an excess of halide salts, forming various coordination compounds. I. M. Korenman has calculated the instability constants for several coordination compounds of silver iodide, concluding that when silver iodide is dissolved in 0.3-1.9 moles of potassium iodide solution, the principal product is $K_3[AgI_4]$ ($K = 3.9 \cdot 10^{-15}$). Taking the figures given for the solubility of silver chloride [10] in solutions of sodium chloride, I. M. Korenman has found that silver chloride dissolves in solutions of up to 0.5 mole per liter of sodium chloride, forming the complex salt $K[AgCl_2]$ ($K[AgCl_2]^- = 2.3 \cdot 10^{-6}$).

These findings enable us to establish the mathematical relationship between the instability constant of a complex ion of the $[AgX_2]^-$ type and the constant for a $[Ag(NH_3)_2X_2]^-$ ion. In effect, the compound $[Ag(NH_3)_2Cl_2]^-$ may be regarded as a product of the action of ammonia upon the $[AgCl_2]^-$ ion in accordance with the following equation: $[AgCl_2]^- + 2NH_3 \rightleftharpoons [Ag(NH_3)_2Cl_2]^-$, whence:

$$K = \frac{[AgCl_2^-][NH_3]^2}{[Ag(NH_3)_2Cl_2^-]} . \quad (7)$$

Dissociation of the complex ion $[AgCl_2]^-$ yields: $[AgCl_2]^- \rightleftharpoons AgCl + Cl^-$, and :

$$K_1 = \frac{\text{"Pr"}\,[Cl^-]}{[AgCl_2^-]} = 2.3 \cdot 10^{-6}, \quad (8)$$

whence

$$[AgCl_2]^- = \frac{\text{"Pr"}\,[Cl^-]}{2.3 \cdot 10^{-6}}. \quad (9)$$

TABLE 5

Calculation of the Instability Constants for the Complex $[Ag(NH_3)_2(IO_3)_2]$

$C_{IO_3^-} \cdot 10^2$ moles/liter	$C_{NH_3} \cdot 10^2$ moles/liter	E, V S. C. E.	E_0, V S. C. E.	$E_0 - E$, V S. C. E.	$C_{Ag^+} \cdot 10^7$ gram-ions/ liter	$B^+ \cdot 10^4$ gram-ions/ liter	$A \cdot 10^4$ moles/ liter	$K \cdot 10^5$
10.00	1.0	0.179	0.372	0.193	2.6	3.0	5.00	4.5
25.00	1.0	0.173	0.372	0.199	2.3	2.3	5.00	5.20
3.8	1.0	0.191	0.379	0.188	4.4	4.2	7.00	2.39
10.00	1.0	0.191	0.379	0.188	4.4	4.2	7.00	6.30
25.00	1.0	0.183	0.379	0.196	3.3	3.2	7.00	6.60
0.5	2.0	0.192	0.413	0.221	4.6	1.7	25.00	1.80
10.00	0.66	0.190	0.205	0.015	–	1.7	3.00	2.23
10.00	0.88	0.186	0.197	0.011	4.0	3.4	4.00	3.7
10.00	1.1	0.179	0.190	0.011	–	3.1	5.00	3.4
10.00	1.32	0.175	0.186	0.011	–	3.8	6.00	6.5
25.00	0.66	0.182	0.205	0.023	–	1.2	3.0	2.0
25.00	0.88	0.175	0.197	0.022	–	1.7	4.0	3.2
25.00	1.1	0.171	0.190	0.023	–	2.4	5.0	5.76

Note. The instability constant of $[Ag(NH_3)_2(IO_3^-)_2]^-$ is estimated as $3.5 \cdot 10^{-5}$.

TABLE 6

Calculation of the Instability Constants for the Complex $[Ag(NH_3)_2(BrO_3)_2]^-$

$C_{BrO_3^-} \cdot 10^2$ moles/liter	$C_{NH_3} \cdot 10^2$ moles/liter	E, V S. C. E.	E_0, V S. C. E.	$E_0 - E$, V S. C. E.	$C_{Ag^+} \cdot 10^7$ gram-ions/ liter	$B^+ \cdot 10^4$ gram-ions/ liter	$A \cdot 10^4$ moles/ liter	$K \cdot 10^5$
3.4	1.0	0.173	0.372	0.199	1.9	2.5	4.4	1.12
25.00	1.0	0.166	0.372	0.206	1.46	1.87	4.4	3.50
0.567	1.0	0.198	0.383	0.185	5.7	6.68	7.7	2.54
3.4	1.0	0.193	0.383	0.190	4.6	5.07	7.7	3.15
0.567	2.0	0.195	0.413	0.218	5.6	21.0	28.0	3.57
10.00	0.44	0.204	0.215	0.011	7.3	1.26	2.0	2.00
10.00	0.66	0.197	0.205	0.008	–	2.2	3.0	6.00
25.00	0.66	0.185	0.205	0.020	–	1.4	3.0	1.90
25.0	0.88	0.178	0.197	0.019	–	1.9	4.0	4.30
25.00	1.10	0.173	0.190	0.017	–	2.5	5.0	6.25

Note. The instability constant of $[Ag(NH_3)_2(BrO_3)_2]^-$ may be taken as $3.44 \cdot 10^{-5}$.

The solubility product "Pr" of silver chloride is $1.69 \cdot 10^{-10}$, that of $[Cl]^-$ equaling the overall concentration of the salt. Inserting the $[AgCl_2]^-$ value in Equation (7), we get:

$$K = \frac{\text{"Pr"}\, C_{salt}\, C^2_{NH_3}}{2.3 \cdot 10^{-6}\, C_{compl.}}. \quad (10)$$

The results of our calculation of K are given in Table 7.

TABLE 7

$C_{NaCl} \cdot 10^2$ moles/liter	a	C_{NH_3} moles/liter	$C_{compl.} \cdot 10^2$ moles/liter	$K \cdot 10^5$
4	0.9	0.4	1.0	4.22
5.7	0.89	0.3	1.0	3.36
7.5	0.87	0.1	0.077	6.6
4.0	0.90	0.4	2.0	2.16
				$K = 4 \cdot 10^{-5}$

TABLE 8

C_{KIO_3} moles/liter	a	$[IO_3^-] \cdot 10^3$ gram-ions/liter	Solubility of $AgIO_3 \cdot 10^5$, moles/liter	$K_1 \cdot 10^6$
0.005	0.960	4.8	6.0	3.15
0.025	0.920	23.00	50.00	1.61
0.50	0.900	45.0	83.0	1.90
				$K_1 = 2.22 \cdot 10^{-6}$

The literature does not give the values of the instability constants for other complex silver ions, such as $[Ag(IO_3)_2]^-$. Hence, calculation of the instability constant of the complex ion $[Ag(IO_3)_2]^-$ required the preliminary study of the solubility of silver iodate in solutions of potassium iodate. These tests were run as follows: Precipitates of silver iodate were transferred to 100-ml measuring flasks, 25 ml of distilled water was added, and given amounts of potassium iodate were introduced. The total volume was raised to 100 ml by adding water, the solution was agitated for 24 hours, and then it was filtered, the iodate in the filtrate being determined iodometrically. The temperature ranged from 20-22° in the various test series.

The calculation was made as follows: the solubility P of silver iodide in a potassium iodide solution may be expressed as:

$$P = [Ag^+] + [Ag(IO_3)_2]^- = \frac{"Pr"}{[IO_3^-]} + [Ag(IO_3)_2]^- . \quad (11)$$

Allowing for dissociation of the complex ion $[Ag(IO_3)_2]^-$ and substituting the appropriate value of the $[Ag(IO_3)_2]^-$ concentration in Equation (11) we find that:

$$P = \frac{"Pr"}{[IO_3^-]} + \frac{"Pr"\,[IO_3^-]}{K_1}, \text{ whence } \quad K_1 = \frac{"Pr"\,[IO_3^-]a}{P - \frac{"Pr"}{[IO_3^-]}} . \quad (12)$$

The means of three determinations are listed in Table 8.

Substituting the values found for K_1 and "Pr", $K_1 = 2.22 \cdot 10^{-6}$ and "Pr" $= 3.5 \cdot 10^{-3}$, in Equation (10), we can compute the constant for $[Ag(NH_3)_2(IO_3)_2]^-$. We find the mean value of the instability constant of the $[Ag(NH_3)_2(IO_3)_2]^-$ ion to be $2 \cdot 10^{-5}$.

Thus, the instability constants of the new coordination compounds, determined potentiometrically and computed from the constants for silver coordination compounds of the $[AgX_2]^-$ type, are of the same order of magnitude, $K = 3 \cdot 10^{-5}$.

Some Theoretical Considerations

The results of research on ternary systems consisting of $AgNO_3 - NH_3 -$ alkali metal halides and other salts convincingly prove that coordination compounds with the general formula of $[Ag(NH_3)_2X_2]^-$, in which the inner sphere of the complex ion contains two ammonia groups in addition to the salt anion, are formed in the solution. We thus get mixed coordination compounds that are fairly stable in solutions containing an excess of ammonia and cannot be isolated in the crystalline state. As Ya. A. Fialkov [11] has said, the inability to isolate a coordination compound from the solutions by crystallization is no proof that there is no such compound in the solution. It must therefore be assumed that the complex salt in solution has a different composition from the coordination compound that could be secured by means of crystallization.

The problem of the connection between the valence of the element and its coordination number is of some interest in view of the fact that mixed coordination compounds of the $[Ag(NH_3)_2X_2]^-$ type, in which the coordination number of the silver is 4 and 2, or 6, 4 and 2 in the case of divalent ions (instead of the coordination number of 2 adopted for silver), are formed in the $AgNO_3 - NH_3 - MeX$ ternary systems.

Grinberg [12], for instance, believes, quite justly, that elements with varying valence should exhibit coordinating ability. Therefore, we must speak of the coordination number of divalent platinum, tetravalent

platinum, monovalent copper, divalent copper, and so forth. It is quite clear that the coordination number is a variable and that a given element is able to exhibit different coordination numbers in different compounds, even when its valence is constant. This circumstance is closely bound up with the conditions under which the coordination compound is produced, with the nature of the reacting ions and coordinated groups, and with other factors as well, such as temperature and pressure.

A number of coordination compounds of silver are known, such as silver ammoniates, silver chlorides, silver cyanides, and the like [13], in which the silver coordination numbers are 1, 2, 3, or 4. Hence, it is quite possible to secure coordination compounds in solution that have several coordination numbers, even for elements with constant valence. We have confirmed this. The basic valence of silver in these compounds remains one, in contrast to the other known silver compounds with a coordination number of 4: $[AgPy_4]^{2+}$, $[AgPhn_2]^{2+}$, [1] in which the silver has a basic valence of 2. As we know, these latter compounds are noted for their high oxidizing ability [14].

The compounds of the $[Ag(NH_3)_2X_2]^-$ ion type that we have synthesized are not oxidants. They must be regarded simply as saturated coordination compounds, whereas the $[Ag(NH_3)_2]^+$, $[AgPy_4]^{2+}$, and other complex ions are unsaturated coordination compounds. One cannot, of course, speak of the identical stability of coordination compounds with a variable coordination number for the central atom. Obviously the compounds in which the central atom exhibits its "normal" coordination number will be most stable. For instance, $[Ag(NH_3)_2]^+$ ($K = 6.8 \cdot 10^{-8}$) is more stable than the complex ion $[Ag(NH_3)_2X_2]^-$ ($K = 3 \cdot 10^{-5}$).

The ions of divalent copper exhibit the coordination numbers 3, 4, and 6, the most stable copper compounds being those with coordination numbers of 3 and 4 for the copper, and those with a coordination number of 6 being least stable. The coordination numbers of zinc and nickel are 6, 4, and 3, the most stable compounds being those with a coordination number of 6, and the least stable those in which the coordination numbers of the zinc or nickel are 4 and 3, and so forth. This is possibly due to the difficulty of securing certain coordination compounds in the free state (different stability of the complex salt in solution and in the solid state).

SUMMARY

1. It has been proved that a mixed complex ion of the $[Ag(NH_3)_2X_2]^-$ type, with the silver having a coordination number of 4, exists in solution.

2. The number of coordinated groups and ions within the inner sphere of the complex ion has been calculated, as well as the instability constants for various complex silver salts.

3. The mean value of the instability constant of a complex ion of the $[Ag(NH_3)_2X_2]^-$ type has been found to be $3 \cdot 10^{-5}$ (X being a monovalent anion).

4. The suggestion is advanced that elements with constant valence, as well as elements with variable valence, may form coordination compounds of the mixed type with different coordination numbers for the central ion. The appearance of elements with differing coordination ability is directly related to the conditions under which the coordination compounds are produced, as well as to the nature of the reacting ions.

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Chair of General Chemistry, Kiev Institute of Medicine

[1] Phn denotes phenanthroline.

SPECTROPHOTOMETRIC INVESTIGATION OF THE INTERACTION OF HALIDES DISSOLVED IN CCl_4

L. S. Lipin

That halides can react with one another has been known for a long time. Gay-Lussac [1], for example, established the existence of compounds of I_2 and Cl_2, while Balard [2, 3] did the same for I_2 and Br_2, Br_2 and Cl_2, etc. Interest in these compounds has continued down to the present, because they are of theoretical as well as practical importance. Doubts have often been expressed, however, concerning the existence of many of these compounds, particularly IBr and BrCl [4, 5, 6] (probably owing to their slight stability [7]). The methods of producing these compounds as well as their refining, are extremely laborious, so that the properties of BrCl, say, are not sufficiently known even now, while IBr forms mixed crystals with the initial components [6] and decomposes during purification. Several papers have been written on the solutions of these compounds. These papers have established the effect of the solvent upon the formation and the behavior of these compounds in solution [22]. We find numerous contradictions in some papers dealing with such thoroughly investigated compounds as ICl. In the older papers [8], for example, we find that when ICl is dissolved in CCl_4, it decomposes as follows: $3ICl \rightarrow I_2 + ICl_3$. Papers published somewhat later, however, state that ICl_3 does not exist at all in CCl_4, breaking down as follows: $ICl_3 \rightarrow ICl + Cl_2$ [9]. Analogous contradictions are to be found in papers dealing with IBr [9, 10].

The direct production of interhalogen compounds in solution, especially in carbon tetrachloride as a "neutral" solvent, should be of particular interest in research into the effect of the solvent upon such compounds [11].

The researches of Gillam and Morton [9] and of Barrat and Stein [12] on such solutions suffer from various deficiencies. The identity of the spectra of solutions of ICl and IBr in CCl_4, prepared by dissolving the previously produced compounds or by directly mixing together equivalent proportions of the respective halides, for instance, is not sufficient proof of the formation of the compounds ICl and IBr in solutions.

The paper on BrCl [12] contains several propositions that must be criticized.

The use of physicochemical analysis in resolving the problem of the interaction of halogens ought to yield more definite results. We have chosen one of the variants of this method, the tested property being the optical density, measured with a spectrophotometer.

We employed the so-called method of "continuous variations" [14, 15, 16], as it is now more and more widely used in the investigation of reactions occurring in solutions [17-21]. Together with the investigation of such systems as ICl, in which the presence of a compound may be felt to be doubtful, our paper serves as further proof of the applicability of the method itself, which, like many another method of physico-chemical analysis, requires careful checking [13]. The method has been described in various papers [14, 15], so that we shall deal with it only briefly.

The Method of Continuous Variations

This method is based upon the determination of a singular point in the function: $\underline{y} = d_C - d_{X_I} - d_{X_{II}}$ (provided ΣM = constant, i.e., the sum of the component concentrations in the mixed solutions must remain constant);

d_C is the optical density of the solution prepared by mixing together Solution I, containing $\underline{v}$ ml of halogen X_I and Solution II, containing $(1-\underline{v})$ ml of halogen X_{II}; d_{X_I} and $d_{X_{II}}$ are the optical densities of the pure components in concentrations corresponding to those in the given mixture.

TABLE 3

λ	ε	λ	ε	λ	ε
750	12	490	724	390	8
700	35	480	568	380	12
650	51	470	328	370	13
600	121	460	234	360	14
580	254	450	164	340	21
550	629	440	92	330	22
540	722	430	49	320	30
530	886	420	25	300	48
520	946	410	14	—	—
500	857	400	10	—	—

There are various references in the literature to the absorption of iodine solutions, but most of them disagree, the most dependable of all the researches being that of Groh and Papp [27], with which our results agree in the main.

Investigation into the Reactions in the I_2-Cl_2; I_2-Br_2 and Br_2-Cl_2 Systems

The results we secured by the spectrophotometric method of "continuous variations" are presented in Figures 1-6.

The values of the function $y = d_c - d_{X_I} - d_{X_{II}}$, expressed in units of optical density ($I = I_0 c^{-\varepsilon dl}$), are plotted along the axis of ordinates with the appropriate sign; the volumetric ratio $\frac{1-v}{v}$ i.e., the ratio of the concentrations of the dissolved halogens, is plotted along the axis of abscissas.

The value of d_c is obtained by measurement, the values of d_{X_I} and $d_{X_{II}}$ being found from the tables (1-3).

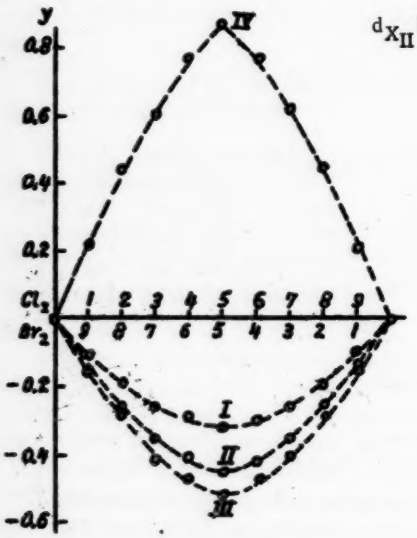

Fig. 5. System Br_2-Cl_2. ΣM = 0.02 mole/liter. I) λ = 520 mμ ; II) λ = 500 mμ ; III) λ = 480 mμ ; IV) λ = 370 mμ (cell length l = 10 mm).

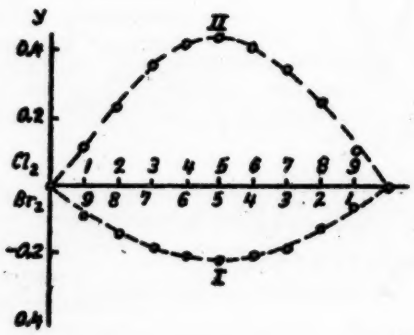

Fig. 6. System Br_2-Cl_2. ΣM = 0.01 mole/liter. I) λ = mμ ; II) λ = 370 mμ (cell length l = 10 mm).

EVALUATION OF RESULTS

Our results indicate beyond the shadow of a doubt that the results are satisfactorily reproducible, this reproducibility being maintained while the total concentration varies, as well as at various wavelengths. The results indicate that the extreme value of the function y occurs at a composition for which the ratio of the initial components is 1:1, which is evidence of the presence of a compound of the $(X_I \cdot X_{II})_n$ type within the system. The applicability of the Lambert-Beer law to these solutions indicates that the number of color centers is unaffected by dilution (i.e., the degree of dissociation remains constant, inasmuch as the initial substances and the reaction products are all colored) [32]. We know that the degree of dissociation may remain practically constant during dilution either when the dissolved compound is very stable or when dissociation is not accompanied by a change in the number of molecules.

Thermodynamical data and various other considerations exclude the first hypothesis, so that we must picture the reaction as follows:

$$(X_I)_2 + (X_{II})_2 \rightleftarrows 2X_I \cdot X_{II},$$

i.e., of all the possible n polymers, only $X_I \cdot X_{II}$ actually exists.

Notwithstanding certain fluctuations of the results toward one side or the other, due to evaporation of the components or to purely experimental errors in measurement, all our curves exhibit the complete symmetry of the function to the right and left of the experimental point. It is not difficult to show, by analysis of the function $\underline{y}$, that this circumstance is one of the proofs of the existence of interaction between the components only in a 1:1 ratio, i.e., the results indicate that no other type of compounds absorbing light in other regions of the spectrum than those we investigated can exist under the specified conditions. It may be added that the extreme points of the ICl and IBr systems represent the intersection of two straight lines, i.e., the extreme point is sharply demarcated. In the BrCl system, however, the extreme point is less sharply marked. This is probably caused by the differing stability of the compounds mentioned, as is borne out by the work of Blair and Jost [7], who give $\alpha = 0.25\%$ as the degree of dissociation for ICl, $\alpha = 0.5\%$ for IBr, and $\alpha = 52.4\%$ for BrCl.

SUMMARY

1. The interaction of halogens dissolved in CCl_4 has been investigated spectrophotometrically for the first time, using the method of "continuous variations", the applicability of this method to instances where the kind of interaction had already been established by other methods also having been checked.

2. The location of the extreme point as well as the symmetry of the function $\underline{y} = \underline{d_c} - d_{X_{II}} - d_{X_{II}}$, leads us to conclude that only one compound, of the $X_I \cdot X_{II}$ type, exists (at the concentrations given) when two halogens dissolved in CCl_4 are mixed together. This type of compound is retained even when one of the components is present in excess.

3. The results, which indicate the presence of compounds of I_2 and Br_2, dissolved in carbon tetrachloride, again remove the doubts that have arisen in the minds of some authors as to the possibility of any such interaction at all.

4. The presence of the compound BrCl in CCl_4 solutions has been convincingly proved for the first time.

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Institute of Chemical Research,
Leningrad State University

THE LAWS GOVERNING CHANGE IN SOLUBILITY

E. I. Akhumov and N. S. Spiro

As we have shown in our preceding paper [5], the following laws hold good for the Raoult coefficient r in a binary system, found from the equation:

$$r = \frac{C}{P_0 - \pi} \tag{1}$$

where P_0 and π are the saturated vapor pressure above the pure solvent and above a solution of concentration C, respectively, for a constant quantity of solvent:

1) For isotherms:

$$r = r_0 + \rho C, \tag{2}$$

where r_0 and ρ are constants.

2) For polytherms:

a) For unsaturated solutions of constant concentration:

$$r = \exp\left(\frac{a}{T} + b\right), \tag{3}$$

b) For saturated solutions.

$$r = \exp\left(\frac{A}{T} + B\right), \tag{4}$$

where a, b, A, and B are constants.

In the present paper which represents a continuation of our previous researches [1,2,3,4,5], we shall discuss the conclusions that stem from deviations from Raoult's law.

Isothermal deviations from Raoult's law for unsaturated solutions in multicomponent systems. We may regard an unsaturated solution of constant concentration as a new solvent, to which all the general laws governing solutions in the binary systems: solvent–solute apply [3].

Equation (2) indicates that the magnitude of the Raoult coefficient changes in binary systems. By analogy we may then write for unsaturated solutions in multicomponent systems:

$$\overline{r} = \overline{r}_0 + \overline{\rho} C, \tag{5}$$

where the symbols with lines over them denote the respective values of the variables in the new solvent, and C is the concentration of the component with which the solution is saturated.

By way of example illustrating the correctness of Equation (5), we cite the data in the ternary system $NaCl-C_{12}H_{22}O_{11}-H_2O$ at 25° [6] for the solubility of $C_{12}H_{22}O_{11}$ (C_2) in $NaCl-H_2O$ solutions in which the NaCl concentration is approximately constant ($C_1 \approx$ const.).

As the experimental findings indicate (Table 1, Figure 1), the Raoult coefficient $\overline{r}$ calculated from Equation (1) is a linear function of the concentration of the variable component C_2 dissolved in a complex solvent ($NaCl-H_2O$):

$$\overline{r} = \overline{r}_0 + \overline{\rho} C_2,$$

thus confirming Equation (5).

Isothermal change of pressure in saturated solvent vapors. It follows from Equations (1) and (2) that:

$$\pi = P_0 - \frac{C}{r_0 + \rho C}, \tag{6}$$

i.e., saturated vapor pressure of the solvent above the solution is a hyperbolic function of the solution concentration expressed for a constant quantity of the solvent.

Rearranging Equation (6), we get:

$$\frac{1}{P_0 - \pi} = \frac{r_0}{C} + \rho, \qquad (7)$$

whence it follows that there is a linear relationship between the reciprocals of the drop in pressure and of the solution concentrations as expressed for a constant quantity of the solvent.

We cite the data for the $K_2SO_4 - H_2O$ and $NaI - H_2O$ systems as examples illustrating the correctness of Equation (7).

The figures for the $K_2SO_4 - H_2O$ system at 30 and 80° [7] are given in Tables 2 and 3 and plotted in Figures 2 and 3 respectively.

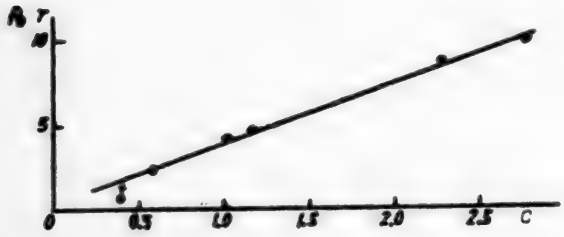

Fig. 1. $NaCl - C_{12}H_{22}O_{11} - H_2O$; 25° isotherm $NaCl:C_1$ = const.

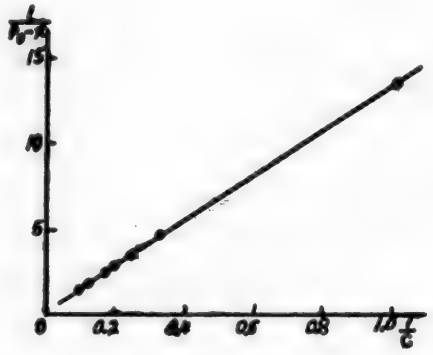

Fig. 2. $K_2SO_4 - H_2O$; 30° isotherm.

The figures for the $NaI - H_2O$ system at 100° [8] are given in Table 4 and plotted in Figure 4.

In these figures the values of the reciprocal concentrations are plotted along the axis of abscissas, with the values of the reciprocal pressure drops of the saturated vapor pressure of the solvent above the solution plotted as ordinates. We see from Figures 2, 3, and 4 that the function is actually linear, i.e., Equation (7) holds.

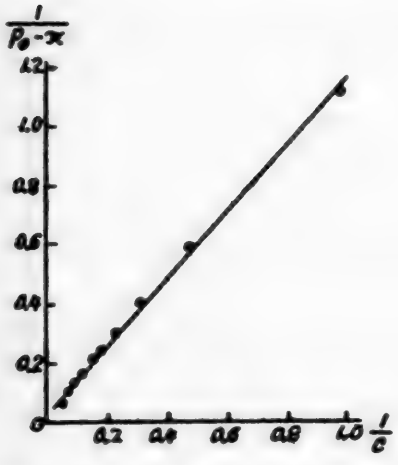

Fig. 3. $K_2SO_4 - H_2O$; 80° isotherm.

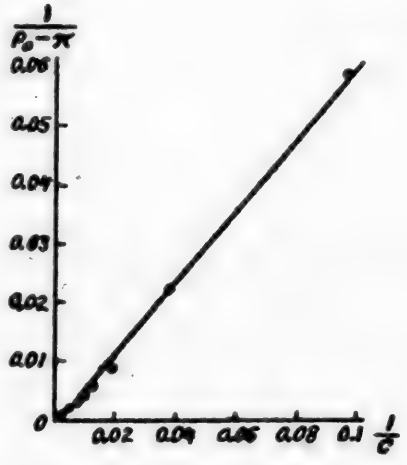

Fig. 4. $NaI - H_2O$; 100° isotherm.

SUMMARY

1. It has been shown that the change in the value of the Raoult coefficient for solutions of a substance dissolved in an unsaturated solution in which the concentration of the other components is constant obeys the same

TABLE 1

$NaCl-C_{12}H_{22}O_{11}-H_2O$ (6) — 25° isotherm

Solution composition in moles/1000 g H_2O		$\frac{P_0}{\pi}$	$\frac{\pi}{P_0}$	$\frac{P_0-\pi}{P_0}$	$P_0 \cdot r$
NaCl C_1	$C_{12}H_{22}O_{11}$ C_2				
6.22	0.40	1.338	0.7474	0.2526	1.584
6.23	0.58	1.340	0.7463	0.2537	2.287
6.33	1.03	1.349	0.7413	0.2587	3.975
6.33	1.18	1.352	0.7396	0.2604	4.531
6.54	2.34	1.388	0.7205	0.2795	8.371
6.63	2.82	1.405	0.7117	0.2883	9.779

TABLE 2

$K_2SO_4-H_2O$ (7) — 30° isotherm

C g/100 g H_2O	π (mm Hg)	$P_0-\pi$ (mm Hg)	$\frac{1}{C}$	$\frac{1}{P_0-\pi}$
0	31.834	0	–	–
1	31.76	0.07	1.000	14.29
2	31.68	0.15	0.500	6.667
3	31.62	0.21	0.333	4.762
4	31.55	0.28	0.250	3.571
5	31.49	0.34	0.200	2.941
6	31.43	0.40	0.167	2.500
8	31.30	0.53	0.125	1.887
10	31.18	0.65	0.100	1.538

laws that hold for binary systems of a solute and a pure solvent.

2. It has been shown that there is a linear relationship between the reciprocals of the drops in pressure and solution concentrations, expressed for a constant quantity of solvent.

TABLE 3

$K_2SO_4-H_2O$ (7) — 80° isotherm

C g/100 g H_2O	π (mm Hg)	$P_0-\pi$ (mm Hg)	$\frac{1}{C}$	$\frac{1}{P_0-\pi}$
0	355.47	0	–	–
1	354.6	0.9	1.000	1.1111
2	353.8	1.7	0.500	0.5882
3	353.0	2.5	0.333	0.4000
4	352.3	3.2	0.250	0.3125
5	351.6	3.9	0.200	0.2564
6	350.9	4.6	0.167	0.2174
8	349.6	5.9	0.125	0.1695
10	348.2	7.3	0.100	0.1370
15	344.7	10.8	0.067	0.0926
20	341.2	14.3	0.050	0.0699

TABLE 4

$NaI-H_2O$ (8) — 100° isotherm

C g/100 g H_2O	π (mm Hg)	$P_0-\pi$ (mm Hg)	$\frac{1}{C}$	$\frac{1}{P_0-\pi}$
0	760	0	–	–
10	743	17	0.10000	0.058823
25	715	45	0.04000	0.022222
50	652	108	0.02000	0.009259
75	581	179	0.01333	0.005587
100	511	249	0.01000	0.004016
125	443.5	316.5	0.00800	0.003160
150	383.5	376.5	0.00667	0.002656
175	332	428	0.00571	0.002336
200	288	472	0.00500	0.002119
225	251.5	508.5	0.00444	0.001967
250	221	539	0.00400	0.001855
275	195.2	564.8	0.00364	0.001770
300	173.3	586.7	0.00333	0.001704

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ELECTRODE POLARIZATION IN THE ELECTROLYSIS OF NICKEL AND COBALT AT A DROPPING MERCURY CATHODE. I.

P. N. Kovalenko and L. S. Nadezhina

In the securing of reproducible, sharply distinct, volt-ampere curves for the electrolysis of metals, especially nickel and cobalt (using a dropping mercury cathode), the properties of the "indifferent" electrolyte in which the polarographic process takes place are of great importance. These properties determine the nature of the polarographic waves, their form and height, the occurrence of maxima, etc. There is no universal polarographic medium, since its choice is frequently dictated by the composition of the substance under test and by the entire setup of the investigation [1].

Nickel and cobalt, elements whose chemical properties are very similar, are deposited at the same potential upon a platinum electrode. The polarographic method enables one to separate their deposition zones by selecting a suitable "indifferent" electrolyte.

Establishing the nature and magnitude of the electrode polarization occurring during the electrolysis of nickel and cobalt in an ammoniacal medium, investigating the influence of oxalate, tartrate, citrate, and salicylate media upon electrode polarization, and investigating the behavior of the ions of these metals in the presence of thiourea, urotropine, and potassium thiocyanate and the influence of these substances upon the nature of the diffusion waves are of considerable interest in selecting the optimum conditions, which make it possible to electrolyze nickel and cobalt together. Research into these problems is the objective of the present paper.

Theoretically, a certain potential $\underline{E}$ must be applied in electrolysis for a metal to begin to be deposited upon the cathode:

$$E = E_0 + \frac{RT}{nF} \ln C. \qquad (1)$$

In practice $\underline{E}$ often exceeds $\underline{E_0}$, the theoretically calculated value, quite considerably. Concentration polarization is very small, usually not exceeding hundredths of a volt [2]. No research has as yet been done on chemical polarization, which greatly affects the electrolysis of nickel and cobalt. Its value often totals hundredths and even tenths of a volt [3].

As we know, the electrolysis of metals consists of several successive stages: the retardation of any one of them may interfere with the securing of an electrochemical reaction product and cause further polarization. At the present time the theory of retarded ion discharge, developed in the Soviet Union by Izgaryshev, Frumkin, and others, must be regarded as the most probable. When metals are electrodeposited on a platinum cathode, chemical polarization may also be caused by a retardation in the rate at which crystal nuclei arise during the formation of the crystal lattice [4,5]. This factor is eliminated when we employ a dropping mercury electrode. The continuous renewal of the mercury surface completely eliminates the effect of any previous processes, while the concentration of the reduced nickel and cobalt ions is so low during polarography that the formation of an amalgam cannot cause chemical polarization, so that the latter must be attributed to action occurring within the solution, i.e., the retarded decomposition of the complex metal ions.

If the ions of the principal electrolyte (the medium) do not react with certain ions, the nature of the principal electrolyte and its concentration (within certain limits: 0.01–0.10 N) have practically no effect upon $E_{1/2}$, since the ionic strength of the solution must be high enough to produce a perceptible deviation of the half-wave potential. Its shift in the given case may be elucidated by analysis of the equation [7]:

$$E_{1/2} = \xi - \frac{0.059}{n} \log \frac{K_s f_a}{K_a f_s} \qquad (2)$$

where K_s and K_a are constants of proportionality in the Ilkovich equation, $605\, nD^{1/2}m^{2/3}\tau^{1/6}$, that describes the diffusion process in the aqueous solution and in mercury; f_s and f_a are the corresponding activity coefficients; and ξ is a constant that depends upon the nature of the substance being reduced. As the ionic strength is increased, the

activity of the ions of the metals being polarographed decreases, and the $E_{1/2}$ is shifted toward the negative. Harden, for example, found that when the concentration of hydrochloric acid was changed twentyfold, the increase in ionic strength produces a shift of the $E_{1/2}$ totaling 10-15 millivolts, which is practically within the limits of experimental error. The change in $E_{1/2}$ may go as high as 100.0-200.0 millivolts when the concentration of the principal electrolyte is varied over a wide range (from 0.01 to 10.0 N) [7]

The presence of dehydrating substances in the solution may also affect the half-wave potential of reducible nickel and cobalt appreciably. When the ions of the "indifferent" electrolyte react with the ions of the metals under study, as is most often manifested by the formation of complex ions, their half-wave potentials shift perceptibly toward the negative by diminishing the actual concentration of free ions [6,8,9]. The concentration of the "indifferent" electrolyte most affects the half-wave potentials of nickel and cobalt in the irreversible process of their reduction. The magnitude of the shift of the half-wave potentials of the nickel and cobalt complex ions is a measure of their stability and makes it possible to establish the structure of the compounds formed by calculating the coordination number (p) from the equation [7]:

$$p = \frac{\Delta E_{1/2}\, n}{0.059 \Delta \log C_X} \qquad (3)$$

where $\Delta E_{1/2}$ is the difference in the half-wave potentials measured at different concentrations of the complex-ion constituent (in volts); n is the number of electrons taking part in the reduction process; and $\Delta \log C_X$ is the difference between the logarithms of the concentration of the complex-ion constituent.

When reversible complex ions of nickel and cobalt are formed, there is no difference between the diffusion current of their electrolytic reduction and that of simple ions, inasmuch as there is practically no difference between the rate of movement of such complex ions and that of simple ions.

In irreversible reduction the amplitude of the diffusion wave is not always linearly proportional to the concentration of the ion being reduced. Soviet researchers, for example, have found that when nickel chloride is reduced in an "indifferent" solution of ammonium chloride containing gelatin, the relationship between the amplitude of the nickel polarographic wave and its concentration in solution is represented by a straight line that does not pass through the origin [10]. In the polarographic determination of nickel in an ammonium cyanide medium, we use an empirical calibration straight line that likewise does not pass through the origin [11]. We used the fundamental equation for a polarographic wave:

$$E_{de} = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_d - i} \qquad (4)$$

where E_{de} is the applied emf (in volts), i is the current at the given point of the volt-ampere curve (in microamperes) and i_d is the limiting current (in microamperes) to test the reversibility of the process of nickel and cobalt reduction.

We have determined the value of the electrode polarization of nickel and of cobalt in all the media specified above, using the slope of the straight line in the graph. From Equation (4) we get:

$$\tan\alpha = \frac{\Delta E_{de}}{\log \frac{i}{i_d - i}} = \frac{0.059}{n}. \qquad (5)$$

The values of the slope found experimentally for the irreversible electrolytic reduction of nickel and cobalt agree with the values calculated theoretically. Whenever the slope found experimentally differs markedly from the theoretical figure, this is evidence of the presence of chemical as well as concentration polarization.

In this research we have investigated electrode polarization in comparatively dilute solutions of "indifferent" electrolytes, which affords several advantages over the use of concentrated solutions: sensitivity of the electrode reaction, choice of conditions for the joint deposition of the metals, and the like.

EXPERIMENTAL

The polarographic solutions we used were $1 \cdot 10^{-6}$ molar solutions of nickel and cobalt sulfate. The pH was measured by the usual electrochemical method, using a hydrogen electrode. We used a 1946 M-7-2000 visual polarograph and a mirror galvanometer with an absolute sensitivity of $1.2 \cdot 10^{-9}$ amp/mm. The distance from the galvanometer mirror to the scale was 0.25 m. Each measurement was repeated 2-3 times at the same galvanometer sensitivity. Two capillaries were used, their constants being given in Table 1.

TABLE 1

Capillary No.	Capillary constant $m^{2/3}\tau^{1/6}$, $mg^{2/3}\ sec^{-1/2}$	Mg. of mercury flowing out per sec, m	Seconds required for the effluence of 1 drop of mercury, t	Remarks
1	2.10	2.61	1.83	Employed in Tests 1-12 of Table 2, Tests 1-11 of Table 3, and in the tests of Fig. 5.
2	1.82	1.89	2.40	Employed in Tests 12-16 of Table 3 and the tests of Fig. 2.

In some instances small maxima appeared in the polarograms; they were suppressed by two drops of 0.5% gelatin or phenol red (per 10.0 ml of solution).

a) Investigation of Electrode Polarization in the Electrolysis of Nickel and Cobalt in Ammoniacal Solutions

We investigated the influence of the following substances upon the volt-ampere curves of nickel and cobalt: 1) ammonium hydroxide; and 2) ammonium chloride containing 1.25 moles of ammonium hydroxide per liter. Our results are given in Table 2.

TABLE 2

Effect of C_{NH_4OH} and C_{NH_4Cl} upon the Amplitude of the Polarographic Wave of Nickel and Cobalt and upon their $E_{1/2}$

Test No.	Concentration		Nickel				Cobalt			
	NH_4OH (mole/liter)	NH_4Cl (mole/liter)	Wave height, mm.	Diffusion current, microamps	$E_{1/2}$, volts	Reduction potential E, volts	Wave height, mm.	Diffusion current, microamps	$E_{1/2}$, volts	Reduction potential E, volts
1	0.1	0.05/0.1	40.0	4.80	−1.00	−0.96	30.0	3.60	−1.430	−1.31
2	0.5	0.05/0.1	41.0	4.92	−1.08	−1.06	55.0	6.60	−1.320	−1.25
3	1.0	0.05/0.1	42.0	5.00	−1.13	−1.09	55.0	6.66	−1.370	−1.33
4	1.5	0.05/0.1	40.0	4.80	−1.16	−1.13	55.0	6.66	−1.380	−1.35
5	2.0	0.05/0.1	37.5	4.50	−1.18	−1.16	57.0	6.84	−1.401	−1.36
6	4.0	0.05/0.1	36.0	4.32	−1.22	−1.17	60.0	7.20	−1.451	−1.40
7	1.25	0.05	43.0	5.16	−1.15	−1.09	55.0	6.60	−1.370	−4.32
8	1.25	0.10	43.0	5.16	−1.15	−1.08	55.5	6.66	−1.370	−1.31
9	1.25	0.20	43.0	5.16	−1.16	−1.10	56.5	6.78	−1.380	−1.31
10	1.25	0.30	42.5	5.12	−1.17	−1.10	56.5	6.78	−1.380	−1.32
11	1.25	0.50	41.0	4.92	−1.19	−1.12	57.5	6.90	−1.390	−1.33
12	1.25	1.0	39.5	4.74	−1.20	−1.13	59.5	7.14	−1.40	−1.34

Note: In Column 3, the figure 0.05 refers to nickel, the 0.1 figure referring to cobalt.

According to the results of Tests 1-6 (Table 2), the nickel diffusion current increases but little at ammonium hydroxide concentrations ranging from 0.1 to 1.0 moles/liter, due to gradual dehydration and the formation of ions whose volume is less. The current reaches a maximum when the ammonium hydroxide concentration is 1 mole/liter, after which it slowly drops with increasing concentration of this complex ion constituent up to 4.0 moles/liter. This is apparently due to an increase in the absolute quantity of complex ammoniacal molecules of nickel, plus an increase in their stability in accordance with the law of chemical equilibrium. As the concentration of ammonium hydroxide is increased, the half-wave potential of nickel is shifted toward the negative, which is evidence of the formation of a complex ion in the solution.

An interesting phenomenon is observed when cobalt is electrolyzed in an ammoniacal medium. As the ammonia concentration is raised from 0.1 to 0.5 mole/liter, the diffusion current of this element rises sharply at first (from 3.60 to 6.60 microamps), though the current rises slowly thereafter as the concentration of this complex-ion constituent is further increased to 4.0 moles/liter, reaching a limiting value of 7.20 microamps. This phenomenon is apparently related to the disintegration of the stable aqueous complex ion of cobalt with the coordination number

6, producing considerable overvoltage during electroreduction, and the formation of an ammoniacal complex ion.

When the hexahydrate complex cobalt ion is converted into an ammoniacal ion, the number of free simple ions of cobalt rises abruptly, and the half-wave potential is sharply shifted toward the positive. Any further increase in the ammonia concentration merely causes a shift in the equilibrium of the ammoniacal complex ions and the simple ions, so that the rise in the negative reduction potential is smooth.

We plotted the curve of $\log \frac{i}{i_d - i}$ as a function of E_{de}, shown in Figure 1, in order to study the nature and magnitude of the electrode polarization occurring in the electrolysis of nickel and cobalt in solutions of a complex-ion constituent. The nickel slope gradually increases as the ammonia concentration is raised (Fig. 1, c). Inasmuch

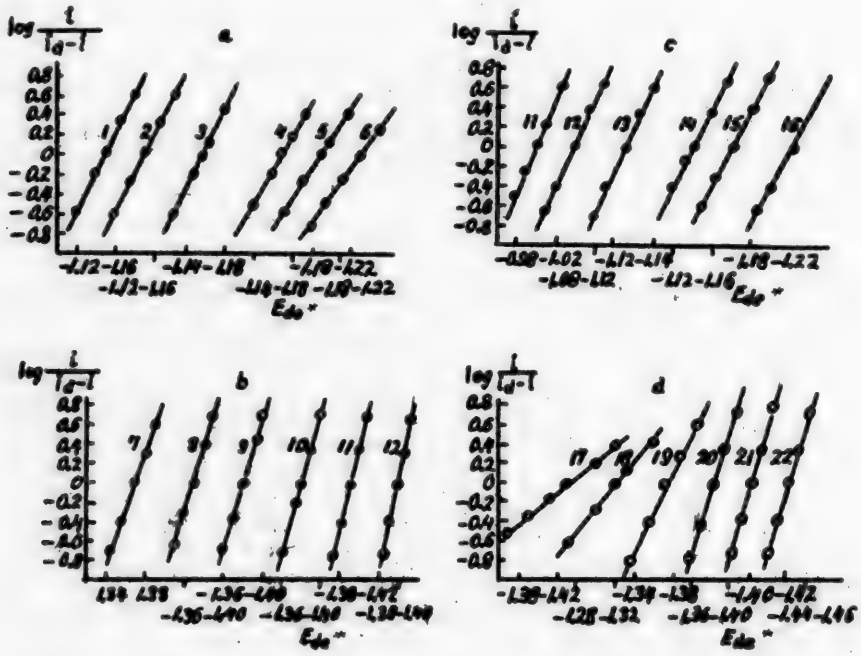

Fig. 1. Electrode polarization in the electrolysis of nickel and cobalt as a function of the concentration of NH_4OH and NH_4Cl. a) Rise in chemical polarization in the electrolysis of nickel as the concentration of NH_4Cl is raised, the NH_4OH concentration being 1.25 moles: 1) 0.05 molar NH_4Cl, tan φ = 0.049; 2) 0.1 molar NH_4Cl, tan φ = 0.050; 3) 0.2 molar NH_4Cl, tan φ = 0.050; 4) 0.3 molar NH_4Cl, tan φ = 0.055; 5) 0.5 molar NH_4Cl, tan φ = 0.065; 6) 1.0 molar NH_4Cl, tan φ = 0.071.

b) Rise in chemical polarization in the electrolysis of cobalt: 7) 0.05 molar NH_4Cl, tan φ = 0.035; 8) 0.1 molar NH_4Cl, tan φ = 0.033; 9) 0.2 molar NH_4Cl, tan φ = 0.032; 10) 0.3 molar NH_4Cl, tan φ = 0.032; 11) 0.5 molar NH_4Cl, tan φ = 0.030; 12) 1.0 molar NH_4Cl, tan φ = 0.030.

c) Increase in the nickel slope with increasing concentration of NH_4OH: 11) 0.1 NH_4OH, tan φ = 0.043; 12) 0.5 molar NH_4OH, tan φ = 0.047; 13) 1 molar NH_4OH, tan φ = 0.048; 14) 1.5 molar NH_4OH, tan φ = 0.050; 15) 2 molar NH_4OH, tan φ = 0.054; 16) 4 molar NH_4OH, tan φ = 0.056.

d) Increase in the nickel slope with increasing concentration of NH_4OH in the reduction of cobalt: 17) 0.1 molar NH_4OH, tan φ = 0.121; 18) 0.5 molar NH_4OH, tan φ = 0.042; 19) 1 molar NH_4OH, tan φ = 0.042; 20) 1.5 molar NH_4OH, tan φ = 0.030; 21) 2 molar NH_4OH, tan φ = 0.030; 22) 4 molar NH_4OH, tan φ = 0.030.

*Standard calomel electrode.

as the retardation of electrolytic reduction at a dropping mercury electrode cannot be attributed to retarded electrocrystallization of the metal, as is the case with a platinum electrode, the difference between the experimentally determined slope and the theoretically calculated value of 0.029 volt may be considered to be the result of retarded decomposition of the complex ammoniacal ion of nickel [13]. The polarographic findings indicate that we can assign the formula of $[Ni(NH_3)_6]^{++}$ to the complex ion, since we got a value approximating six when we computed the coordination number from Equation 3 (Table 4).

TABLE 3

Effect of the Concentration of Ammonium Oxalate and of the Solution pH upon the Diffusion Current of Nickel and Cobalt and upon their $E_{1/2}$

Test No.	Concentration NH_4OH (mole/liter)	Concentration Ammonium oxalate (mole/liter)	Solution pH	Nickel: Wave height, mm.	Nickel: Diffusion current, microamps	Nickel: $E_{1/2}$ volts	Nickel: Reduction potential E, volts	Cobalt: Wave height, mm.	Cobalt: Diffusion current, microamps	Cobalt: $E_{1/2}$ volts	Cobalt: Reduction potential E, volts
1	–	0.05	5.1	35.0	1.68	−0.95	−0.75	43.0	2.06	−1.08	−0.87
2	–	0.05	6.0	36.0	1.72	−1.02	−0.80	45.0	2.16	−1.08	−0.89
3	–	0.05	7.0	37.0	1.78	−1.08	−0.85	47.0	2.26	−1.08	−0.89
4	–	0.05	8.0	40.0	1.92	−1.18	−0.88	49.0	2.35	−1.09	−0.90
5	–	0.05	10.0	70.0	3.36	−1.33	−1.20	112.0	5.38	−1.36	−1.25
6	–	0.01	10.0	19.0	2.28	−1.19	−1.11	–	–	–	–
7	–	0.05	10.0	28.5	3.42	−1.31	−1.22	49.0	5.88	−1.35	−1.25
8	–	0.10	10.0	38.0	4.56	−1.36	−1.29	60.0	7.20	−1.39	−1.29
9	–	0.15	10.0	40.0	4.80	−1.377	−1.33	56.0	6.72	−1.40	−1.32
10	–	0.20	10.0	39.0	4.68	−1.38	−1.34	50.0	6.00	−1.40	−1.33
11	–	0.30	10.0	37.0	4.56	−1.38	−1.34	45.5	5.46	−1.45	−1.40
12	0.05	0.10	–	20.0	2.40	−1.15	−1.08	31.5	3.78	−1.40	−1.33
13	0.10	0.10	–	25.0	3.00	−1.13	−1.06	32.5	3.90	−1.38	−1.32
14	0.50	0.10	–	26.0	3.12	−1.15	−1.09	33.0	3.96	−1.39	−1.34
15	1.00	0.10	–	26.5	3.18	−1.15	−1.08	34.0	4.08	−1.40	−1.35
16	1.50	0.10	–	27.0	3.28	−1.19	−1.10	34.5	4.14	−1.43	−1.38

Note: During polarography of solutions, the galvanometer sensitivity was S = 1/10 (in Tests 1-5); in all other tests S = 1/25.

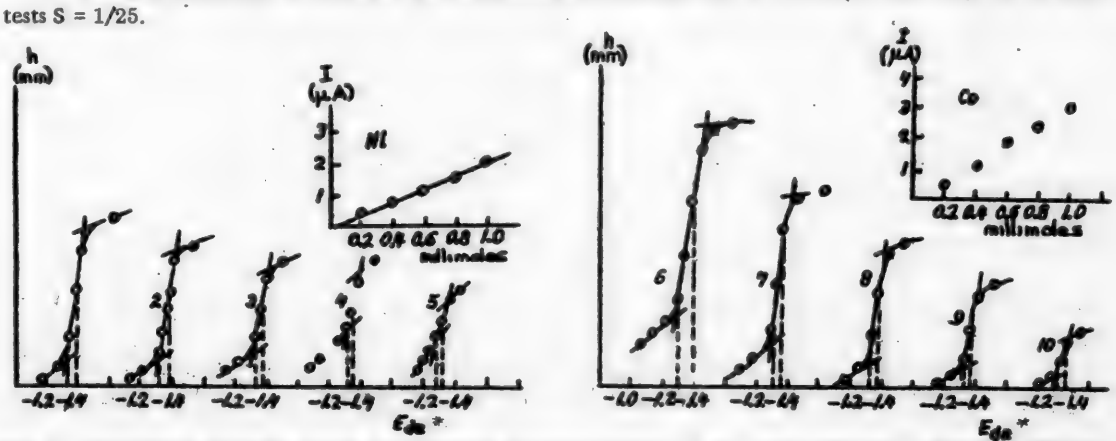

Fig. 2. Calibration lines for nickel and cobalt in their electrolysis in 0.1 molar NH_4Cl + 1.25 molar NH_4OH.

* Standard calomel electrode.

The curves showing the variation of $\frac{i}{i_d - i}$ with E_{de} in the polarography of cobalt (Fig. 1, d) are evidence of appreciable polarization at low ammonia concentrations; raising the concentration of the ammonia solution diminishes the chemical polarization at the cathode. There is no chemical polarization present in a 1.5-molar solution of ammonium hydroxide; hence, the hexahydrate complex ion of cobalt causes greater retardation of electrolytic reduction than does the ammonia complex ion. Other research workers [16] have also observed a decrease in chemical polarization in electrolysis during the reduction of ammoniacal complex ions, as compared to the hexahydrate cobalt ion.

The coordination number was found to approximate six (Table 4); hence, we can say that there are hexammine cobaltic ions in the solution. The slight discrepancy between the values of the coordination number found by polarography in ammonia and the theoretical figure of 6 may be attributed to the incomplete transformation of the complex hexahydrate ion into a hexammine ion with a coordination number of 6. Some ions of other composition

TABLE 4

Coordination Numbers of Complex Ions of Nickel and Cobalt in Ammonia and Oxalate Solutions

Complex-ion constituents	Ratio of concentrations of complex-ion constituents (C_2/C_1)	Nickel		Cobalt	
		Difference of half-wave potentials, $\Delta E_{1/2}$	Coordination number, p	Difference of half-wave potentials, $\Delta E_{1/2}$	Coordination number, p
Ammonia	0.5/0.1	0.080	3.90	–	–
	1.0/0.5	0.050	5.72	0.05	5.72
	2.0/1.5	0.021	5.70	0.021	5.70
	4.0/2.0	–	–	0.05	5.72
Ammonium oxalate at pH = 10	0.10/0.05	0.05	5.72	–	–
	0.15/0.10	0.017	3.25	0.01	1.98

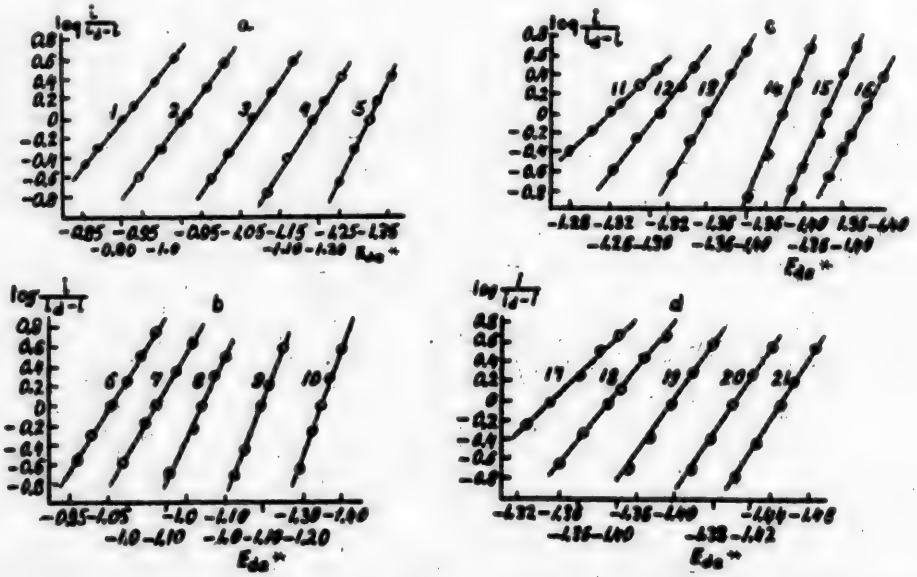

Fig. 3. Variation of the electrode polarization of nickel and cobalt with the pH and the concentration of ammonium oxalate.

a) Nickel slopes at a $(NH_4)_2C_2O_4$ concentration of 0.05 mole and various solution pH: 1) pH = 5, tan φ = 0.217; 2) pH = 6, tan φ = 0.190; 3) pH = 7, tan φ = 0.189; 4) pH = 8, tan φ = 0.167; 5) pH = 10, tan φ = 0.123.

b) Nickel slopes at a $(NH_4)_2C_2O_4$ concentration of 0.05 mole and various solution pH, for the electrolysis of cobalt: 6) pH = 5, tan φ = 0.159; 7) pH = 6, tan φ = 0.149; 8) pH = 7, tan φ = 0.120; 9) pH = 8, tan φ = 0.093; 10) pH = 10, tan φ = 0.089.

c) Effect of $(NH_4)_2C_2O_4$ concentration upon the electrode polarization of nickel at a pH = 10; 11) 0.01 molar $(NH_4)_2C_2O_4$, tan φ = 0.123; 12) 0.05 molar $(NH_4)_2C_2O_4$, tan φ = 0.043; 13) 0.1 molar $(NH_4)_2C_2O_4$, tan φ = 0.044; 14) 0.15 molar $(NH_4)_2C_2O_4$, tan φ = 0.035; 15) 0.2 molar $(NH_4)_2C_2O_4$, tan φ = 0.039; 16) 0.3 molar $(NH_4)_2C_2O_4$, tan φ = 0.047.

d) Effect of $(NH_4)_2C_2O_4$ concentration upon the electrode polarization of nickel a at a pH = 10, for the electrolysis of cobalt: 17) 0.05 molar $(NH_4)_2C_2O_4$, tan φ = 0.090; 18) 0.1 molar $(NH_4)_2C_2O_4$, tan φ = 0.039; 19) 0.15 molar $(NH_4)_2C_2O_4$, tan φ = 0.047; 20) 0.2 molar $(NH_4)_2C_2O_4$, tan φ = 0.062; 21) 0.3 molar $(NH_4)_2C_2O_4$, tan φ = 0.060.

*Standard calomel electrode.

may be formed, in which not all the 6 coordinated positions are filled by ammonia molecules, one or more of the positions being occupied by polar molecules of water, as in the complexes of the $[CO(NH_3)_n(H_2O)_m]^{\cdot\cdot}$, type, where the sum of n and m totals 6. Mendeleev [14], Grinberg [15], and others have commented on the possibility that such complex ions exist.

When the concentration of ammonium chloride is raised, while the ammonia concentration of 1.25 moles/liter is held constant, practically no change occurs in the diffusion current of nickel or cobalt; only at concentrations of ammonium chloride ranging from 0.3 to 1.0 mole/liter does the height of the nickel polarographic wave drop, the height of the cobalt wave rising slightly due to a change in the mobility of the complex molecules. Our findings on the decrease in the amplitude of the polarographic waves of nickel agree with the findings of Usatenko and Lyalikov, who state that ammonium chloride in the presence of ammonia almost does not suppress the wave of this metal at all [11].

Under these conditions the half-wave potentials of nickel and cobalt are gradually made more negative, which may be attributed to a shift of the equilibrium between the hexammine ions and the simple ions toward a decrease in the number of the latter, as well as to an increase in the ionic strength of the solution as the concentration of the ammonium chloride is increased. When we examine the curve of $\log \frac{i}{i_d - i}$ as a function of E_{de}, we see how chemical polarization gradually and slowly increases with an increase in the concentration of NH_4Cl during the electrolysis of nickel (Figure 1, a); at the same time, Figure 1, b shows that the slopes found from the cobalt polarograms are in good agreement with the theoretical value, 0.029, which is evidence of the reversibility of the electrode reaction involved in the reduction of cobalt.

As a result of our study of electrode polarization during the electrolysis of nickel and cobalt in a buffer solution of NH_4OH and NH_4Cl we have found the optimum conditions at which the diffusion current is a maximum, the polarographic wave is most distinct, and the reproducibility of the polarographic measurements is at its best. These were the conditions used in plotting the straight lines for these metals at concentrations ranging from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-4}$ mole/liter (Figure 2). It has been found that diffusion current is a linear function of the concentration of the metals tested. This linearity is disturbed when the ammonium chloride solution contains no ammonia, the calibration straight line no longer passing through the origin.

b) Electrode Polarization in the Electrolysis of Nickel and Cobalt in Oxalate and Ammoniacal Oxalate Solutions

Polarography of nickel and cobalt in a 0.05 molar solution of ammonium oxalate could be done only at values of the solution pH in excess of 4. When the pH was lower, the polarographic waves of the metals under study ran together with the hydrogen waves. The polarographic data are given in Table 3.

As Table 3 indicates (Tests 1-5), changing the pH from 5.1 to 8.0 raises the diffusion current only slightly for both metals, while raising the pH from 8.0 to 10.0 produces an abrupt rise in the current of approximately 100% in the electrolytic reduction of nickel and of 150% in the reduction of cobalt. When the hydrogen ion concentration is lowered to a certain limit (pH 5.0 to 8.0), the half-wave potential becomes slightly more negative. After this limit, raising the pH (from 8.0 to 10.0) produces a sharp increase in potential. At the same time the polarogram slopes decrease with a diminishing hydrogen ion concentration, which is evidence of a decrease in chemical polarization (Figure 3,a). Apparently, the transition from an acid medium to an alkaline one involves the production of complex ions of different composition, causing a sharp rise in the diffusion current and a shift in the half-wave potential (Table 3).

We also made a study of the behavior of cobalt and nickel ions when the concentration of ammonium oxalate was varied (Table 3) while the pH was held constant at 10.0. Increasing the concentration of the ammonium oxalate solution from 0.01 to 0.10 mole/liter resulted in a sharp increase in the nickel and cobalt diffusion current and in an appreciable shift of their half-wave potentials toward the negative. Whereas a further increase in the ammonium oxalate concentration to 0.30 mole/liter produced practically no rise in the diffusion current during the reduction of nickel, the i_d dropped appreciably during the reduction of cobalt, exhibiting a maximum in a 0.1 molar solution of ammonium oxalate. The cobalt diffusion current vanished in a saturated solution of the oxalate. The half-wave potential, which remained practically constant in the case of nickel, decreased, even though only slightly, in the case of cobalt. The slopes of the nickel polarograms for various concentrations of ammonium oxalate are reproduced in Figure 3,c. These slopes indicate that, in conformity with the foregoing assertions concerning the changes in i_d and $E_{1/2}$, the chemical polarization diminishes as the concentration of the tested complex-ion constituent is raised to 0.10 mole/liter, this polarization practically disappearing in a 0.15 molar solution and rising again as the ammonium oxalate concentration is raised still higher. The decrease in chemical polarization as the ammonium oxalate concentration is raised is due to dehydration of the complex nickel hexahydrate ion, while the rise in the i_d is due to a decrease in the volume of the resulting complex nickel oxalate ion because of the rearrangement of the coordinated groups in the inner sphere of the complex ion. Calculation of the coordination

number yielded values of 6 and 3 (Table 4). The transformation of the complex nickel ion with coordination number 6 into a complex ion with coordination number 3 (Table 4) is due to a change in the inner sphere of the complex ion. It may be regarded as established that the C_2O_4'' group usually occupies two coordination positions in the formation of stable coordination compounds, the compounds in which the oxalate ion occupies one coordination position being less stable and being readily converted into a more stable form. In this case, a complex nickel ion in which all six positions are occupied by C_2O_4'' groups is formed at comparatively low concentrations of ammonium oxalate. As the concentration of oxalate ions is increased, the stability of the complex ion grows, due to the formation of a compound in which each C_2O_4'' group occupies two coordination positions. Thus we get the value of 3 when we calculate the p for complex ions that are formed in solutions containing a high concentration of ammonium oxalate.

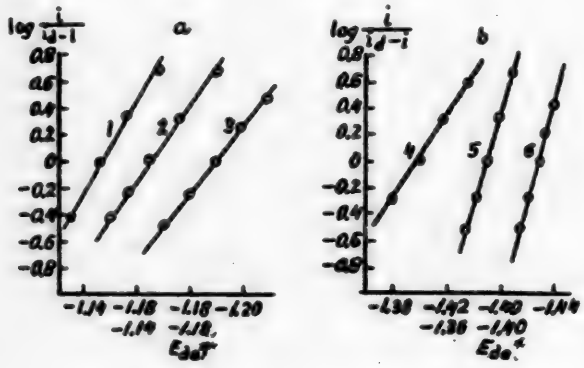

Fig. 4. Variation of the slope in the electrolysis of nickel and cobalt in an ammonia-oxalate solution whose $(NH_4)_2C_2O_4$ concentration = 0.1 mole/liter.

a) Electrolysis of nickel: 1) 0.05 molar NH_4OH, tan φ = 0.066; 2) 0.5 molar NH_4OH, tan φ = 0.074; 3) 1.5 molar NH_4OH, tan φ = 0.080.

b) Electrolysis of cobalt: 4) 0.05 molar NH_4OH, tan φ = 0.062; 5) 0.5 molar NH_4OH, tan φ = 0.029; 6) 1.5 molar NH_4OH, tan φ = 0.029.

*Standard calomel electrode.

The slopes of the cobalt polarograms (Figure 3,d) are evidence of a decrease in cathodic polarization as the concentration of ammonium oxalate rises. This decrease in polarization during the electrolysis of cobalt does not, however, attain the level required for reversibility of the reaction. In the electrolytic reduction of nickel, however, the electrode reaction becomes reversible under these conditions.

Thus, these findings indicate that the complex cobalt hexahydrate ion is decomposed more slowly than the ammonia and oxalate ions (at a pH = 10.0).

When we computed the coordination number of cobalt we got values that were close to 2 (Table 4). Here again, we have a rearrangement within the inner sphere of the complex ion, resulting in a lowering of the coordination number to 2. The circumstance that the figure of 4.50 calculated from the experimental data differs substantially from the value of 4.0 is due, in our opinion, to the presence of a small percentage of complex ions with coordination number 6 in the solution.

We likewise investigated the variation of the nickel and cobalt vole-ampere curves with the ammonia concentration when 0.1 mole/liter of ammonium oxalate was present. The results of our experiments are given in Table 3 (Tests 12-16). As we see from these experimental figures, the nickel and cobalt $E_{1/2}$ does not change perceptibly as the ammonia concentration is increased; the diffusion current of both metals, however, rises, even though only slightly, due to the production of more highly mobile ions. As in the instances of the electrolysis of nickel in a NH_4OH-NH_4Cl buffer solution considered previously, the polarization rises with an increase in the concentration of ammonium hydroxide, this polarization being most pronounced in an ammonia-oxalate solution (Figure 4,a). As for the polarization occurring in the electrolysis of cobalt in this same basic solution, the slopes indicate that chemical polarization is suppressed when the ammonia concentration is sufficiently high (Figure 4,b). Thus it is ammonia that exerts the principal influence upon the volt-ampere curve in an ammonia-oxalate medium. Calibration lines were plotted for both metals at concentrations ranging from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-4}$ mole/liter, and at the optimum conditions of a pH of 10 and an approximately 0.125 molar solution of ammonium oxalate. We found that the nickel and cobalt i_d was a linear function of the ammonium oxalate concentration, the straight line passing through the origin (Figure 5).

SUMMARY

1. A study has been made of the nature of electrode polarization in the electrolysis of nickel and cobalt sulfates at a dropping mercury electrode with different complex-ion constituents present. It has been found that an

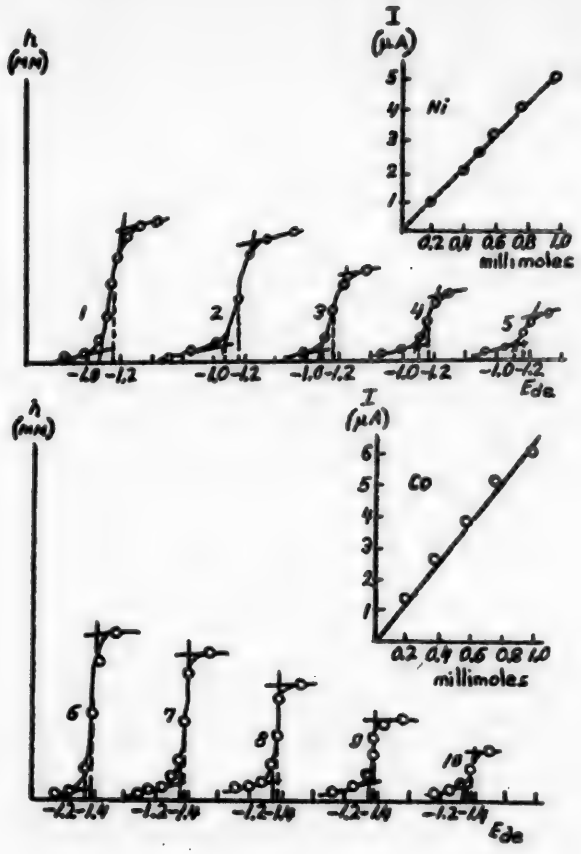

Fig. 5. Calibration lines of nickel and cobalt in their electrolysis in a 0.125 molar solution of $(NH_4)_2C_2O_4$ at a pH = 10.

irreversible electrolytic reduction of nickel and cobalt takes place in some buffer mixtures of NH_4OH and NH_4Cl and ammonia-oxalate solutions.

2. It is suggested that the reason for the irreversible reduction of nickel and cobalt at a dropping mercury electrode from complex ions formed in the media specified above is the stable hydration that prevents the instantaneous decomposition of the complex ion. When the hydrate layer is broken down, even when more stable but less highly hydrated coordination compounds are formed, the chemical polarization is either diminished or disappears completely, which is evidence of the occurrence of a reversible electrolytic reduction of the nickel and cobalt ions.

3. It has been shown experimentally that when NH_4OH is present (within a certain concentration range), the complex nickel and cobalt oxalate ions break down, forming ammonia ions.

4. The variation of the amplitude of the nickel and cobalt diffusion waves with their concentration in the media we have tested has been checked, and it has been established that the equation: $\underline{i_d} = \underline{KC}$ holds under these conditions.

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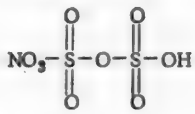
Rostov-on-Don State University

STUDY AND CLASSIFICATION OF THE COMPOUNDS IN THE SULFUR TRIOXIDE–NITROGEN PENTOXIDE–WATER SYSTEM

I. I. Zaslavsky, O. M. Klimova, and L. V. Guskova

It has been definitely established by now that three individual compounds of definite chemical composition exist in the solid crystalline state, all containing sulfur trioxide in addition to nitrogen pentoxide.

The pioneer in the investigation of compounds of this type was Weber [1], who isolated two crystalline compounds as far back as 1864: $N_2O_5 \cdot 4SO_3 \cdot H_2O$ and $N_2O_5 \cdot 4SO_3 \cdot 3H_2O$. The first of these compounds, $N_2O_5 \cdot 4SO_3 \cdot H_2O$, or, writing it differently, $HNO_3 \cdot 2SO_3$, was again produced and described in 1949 by Amelin and Borodastova [2]. The two authors regard the compound they synthesized as a nitratopyrosulfonic acid and assign it the following structural formula:



The crystals had a m.p. of + 106.5°.

In the same year, 1949, Dode and Pascard [3] synthesized Weber's other compound: $N_2O_5 \cdot 4SO_3 \cdot 3H_2O$, which the authors assert "had never been synthesized since Weber's time in 1864", and "about which practically nothing is known, neither its physical and chemical properties nor its structure." Dode effected their synthesis under complicated experimental conditions, using low temperatures and pressures.

Dode and Pascard found the melting point of the compound they had produced was +32°, though they advanced no structural formula for it. Lastly, in 1907 Pictet and Karl [4] synthesized and described the anhydrous compound $N_2O_5 \cdot 4SO_3$, which they called nitrilotetrasulfate. This compound proved to be highly stable. Its melting point was +124° and its boiling point +220°. The authors assigned it the following structural formula:

$$O_2N-O-SO_2-O-SO_2-O-SO_2-O-SO_2-O-NO_2.$$

All the three specified compounds are apparently representatives of a single type:

$$N_2O_5 \cdot 4SO_3 \cdot \underline{m}H_2O, \qquad (1)$$

where $\underline{m}$ is zero, one, and three.

Any further increase in $\underline{m}$, i.e., in the number of water molecules added, results in the formation of a system that is liquid at ordinary temperatures, in which Hantzsch [5], Usanovich [6], and other researchers, including ourselves [7], have succeeded in detecting a partially dissociated individual compound of the same type, in which $\underline{m}$ equals five, i.e., $N_2O_5 \cdot 4SO_3 \cdot 5H_2O$ or $N(OH)_3(HSO_4)_2$.

Moreover, we have succeeded in experimentally proving, by the iodometric method, that a compound of a totally different type:

$$N_2O_5 \cdot 2SO_3 \cdot nH_2O, \qquad (2)$$

where $\underline{n} = 3$ to wit: $N_2O_5 \cdot 2SO_3 \cdot 3H_2O$, or according to Hantzsch, $[NO_3H_2]HSO_4$, is present in concentrated liquid sulfuric-nitric mixtures.

In the experimental section of this paper we report some further results of our investigations of the N_2O_5–SO_3–H_2O ternary system through as wide a range as possible of its existence in the liquid state. We used the viscosimetric method of physicochemical analysis in these investigations.

EXPERIMENTAL

Using the viscosity method proved to be quite feasible, since even those compounds in the $N_2O_5-SO_3-H_2O$ system that are solid at room temperature, which fuse when the temperature is raised, exhibit an exceptional tendency toward supercooling, persisting in the liquid state even at temperatures that are dozens of degrees below the melting point.

As we know, another feature of the viscosity method is the fact that this method may be employed to confirm the presence of only a single compound in the system in question, even when other methods definitely establish the presence of several coordination compounds. Apparently, viscosimetry detects only that compound, of those formed within the system, which is partially dissociated into its constituent molecules to the least degree.

The results of our experimental measurements of the viscosity in the nitric acid–pyrosulfuric acid at the three temperatures of 0, 20, 30.2° are listed in Table 1 and illustrated in Figure 1.

As we see from the data, the viscosity maximum at 0 and 20° corresponds to a composition of:

$$HNO_3 \cdot H_2S_2O_7 \text{ or } N_2O_5 \cdot 4SO_3 \cdot 3H_2O$$

The viscosity maximum at 30.2° is shifted somewhat toward pyrosulfuric acid, i.e., the more viscous component, which must be related to the increasing dissociation of the compound. Hence, the existence of the compound $N_2O_5 \cdot 4SO_3 \cdot 3H_2O$ in the liquid as well as the solid state must be regarded as definitely established.

TABLE 1

Viscosity of the $HNO_3-H_2S_2O_7$ System

HNO_3		Viscosity, centipoises		
% by weight	Molar %	0°	20°	30.2°
0.0	0.0	–	57.2	37.5
7.4	18.5	–	91.2	56.9
15.0	33.3	–	97.8	72.6
19.8	41.1	543.4	138.8	81.8
23.1	46.0	–	154.2	**93.9**
26.2	50.1	**574.9**	**161.9**	86.7
30.4	55.2	–	117.7	68.9
31.9	57.1	–	103.5	62.6
35.9	61.3	231.3	72.8	45.9
40.1	65.4	156.8	53.4	34.2
45.1	69.9	95.7	34.5	23.5
50.2	74.0	58.2	23.1	16.1
60.1	81.0	25.1	11.3	8.3
70.0	86.8	11.8	5.9	4.9
80.0	91.9	5.6	3.1	2.4
90.0	96.2	2.6	1.6	1.3

TABLE 2

Viscosity of the HNO_3-SO_3 System at 30.2°

HNO_3		Viscosity, centipoises
% by wt.	Molar %	
14.6	17.8	234.7
21.7	26.0	1046.0
25.6	29.7	**1074.3**
27.6	32.6	971.6
33.5	39.0	921.4
45.0	51.0	410.4
69.9	74.7	12.4
80.9	84.4	3.5
95.1	93.6	1.2

TABLE 3

Specific Viscosity of the $HNO_3-H_2SO_4$ System at 20.8°

HNO_3		Specific gravity, $d_4^{20.8}$	Viscosity, centipoises
% by weight	Molar %		
0.0	**0.0**	1.8300	23.2
8.5	12.7	1.8744	29.2
13.1	19.0	1.8683	30.5
17.1	24.4	1.8641	30.6
20.3	28.4	1.8534	29.0
22.8	31.4	1.8475	27.8
30.9	41.0	1.8206	22.0
38.2	49.0	1.7955	16.8
45.2	56.3	1.7692	13.4
55.3	65.8	1.7305	8.5
67.5	76.4	1.6794	4.7
76.6	83.6	1.6401	2.9
88.5	92.3	1.5812	1.6
100.0	100.0	1.5113	0.9

Another representative of the same stable $N_2O_5 \cdot 4SO_3 \cdot mH_2O$ type may be detected in a no less distinct form when we investigate the internal friction in the HNO_3-SO_3 system (Table 2 and Figure 2). Due to the high temperature (30.2°), the viscosity maximum in this system is shifted somewhat toward the more viscous component SO_3, but the very high relative and absolute values of the maximum viscosity are evidence of the intensity of the chemical interaction between the components. We have not yet been able to measure the internal friction at a lower temperature.

Thus, the existence of a $HNO_3 \cdot 2SO_3$ or a $N_2O_5 \cdot 4SO_3 \cdot H_2O$ compound in the liquid state as well as in the solid state must also be regarded as fully established.

When we compare the maximum values of viscosity at the same temperature (30.2°) in the HNO_3-SO_3 system (Table 2), and the $HNO_3-H_2S_2O_7$ system (Table 1), we notice the rapid drop in the absolute

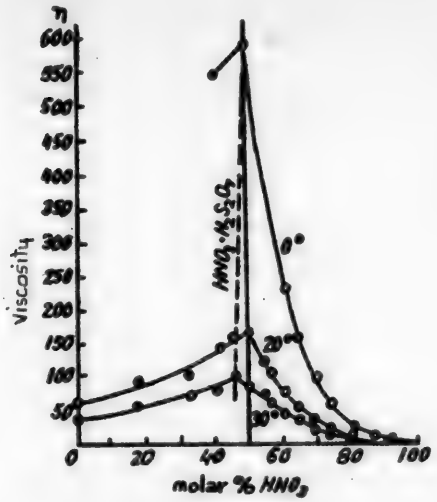


Fig. 1. Viscosity of the $HNO_3-H_2S_2O_7$ System.

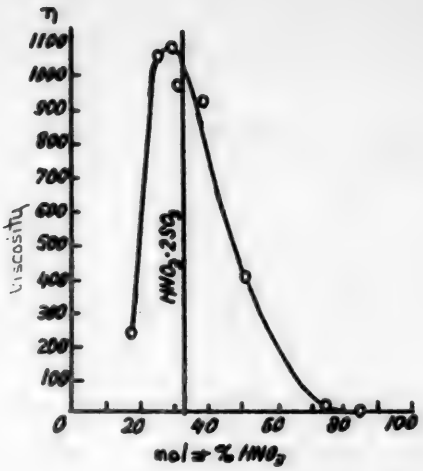


Fig. 2. Viscosity of the HNO_3-SO_3 System at 30.2°.

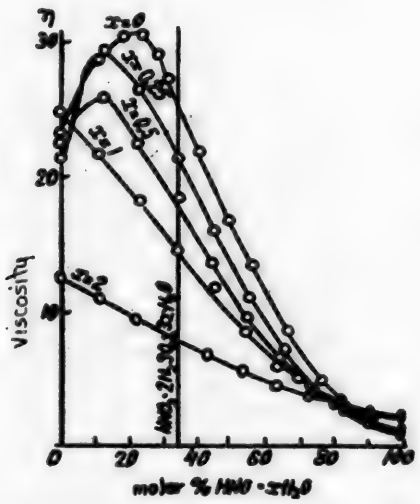


Fig. 3. Viscosity of the $HNO_3 \cdot xH_2O-H_2SO_4 \cdot xH_2O$ System at 20.8°.

viscosity as the percentage of water in the system increases (1074.3 and 93.9 centipoises). This is probably due to a decrease in the stability of the individual members of the $N_2O_5 \cdot 4SO_3 \cdot mH_2O$ series as the value of the coefficient m rises, i.e., as the number of molecules of water entering into the composition of the molecule of the complex compound is increased.

We ran a series of experiments in which we measured the viscosity of the $HNO_3 \cdot xH_2O-H_2SO_4 \cdot xH_2O$ system, where x = 0, 0.25, 0.5, 1.0 and 2.0, to shed more light on this question.

Our results are listed in Tables 3-7 and illustrated in Figure 3.

Classification of the compounds found.

Present-day information on the properties of mixtures of nitric acid with sulfuric acid and oleums of various concentrations [8], based chiefly upon study of the products of electrolysis and analysis of Raman spectra, indicates that these mixtures contain nitrogen-containing cations and anions with the composition of HSO_4^- and $HS_2O_7^-$. Collating these data with the research results set forth in the present paper, we shall attempt to suggest a classification of the various members of the $N_2O_5 \cdot 4SO_3 \cdot mH_2O$ series whose existence has been most reliably established.

We now believe the individual members of this series to be the following individual saltlike compounds:

1. $N_2O_5 \cdot 4SO_3$.

Pictet and Karl called this highly stable compound nitriliotetrasulfate. We think that the structure of this substance, which is crystalline at room temperature, is like that of potassium tetrachromate, so that we shall call it nitronium tetrasulfate.

2. $N_2O_5 \cdot 4SO_3 \cdot H_2O$

Amelin and Borodastova have called this compound nitratopyrosulfonic acid monohydrate. We have also synthesized the beautifully formed crystals of this hydrate. What is more, we have established the presence of this compound beyond the shadow of a doubt in our study of the liquid system HNO_3-SO_3 not only by the volumetric

TABLE 4

Specific Viscosity of the $HNO_3 \cdot 0.25\ H_2O - H_2SO_4 \cdot 0.25 H_2O$ System at 20.8°

$HNO_3 \cdot 0.25H_2O$ % by weight	$HNO_3 \cdot 0.25H_2O$ Molar %	Specific gravity, $d_4^{20.8}$	Viscosity, centipoises
0.0	0	1.8342	21.6
8.4	12.2	1.8476	29.9
17.0	23.7	1.8230	26.8
25.9	34.7	1.7937	21.6
35.2	45.2	1.7596	16.0
44.9	55.3	1.7255	11.1
54.9	64.9	1.6861	7.3
65.2	74.0	1.6436	5.1
76.4	83.1	1.5954	2.7
87.9	91.7	1.5430	1.6
100.0	100.0	1.4907	1.1

TABLE 5

Specific Viscosity of the $HNO_3 \cdot 0.5H_2O - H_2SO_4 \cdot 0.5H_2O$ System at 20.8°

$HNO_3 \cdot 0.5H_2O$ % by weight	$HNO_3 \cdot 0.5H_2O$ Molar %	Specific gravity, $d_4^{20.8}$	Viscosity, centipoises
0.0	0.0	1.8230	22.9
8.8	12.6	1.8112	26.1
16.9	23.2	1.7854	22.6
25.9	34.2	1.7552	18.1
35.2	44.7	1.7229	13.7
44.7	54.2	1.6863	9.5
54.8	64.4	1.6474	6.8
65.3	73.7	1.6068	4.3
76.0	82.5	1.5673	2.9
87.8	91.4	1.5228	1.9
100.0	100.0	1.4762	1.3

TABLE 6

Specific Viscosity of the $HNO_3 \cdot H_2O - H_2SO_4 \cdot H_2O$ System at 20.8°

$HNO_3 \cdot H_2O$ % by weight	$HNO_3 \cdot H_2O$ Molar %	Specific gravity, $d_4^{20.8}$	Viscosity, centipoises
0.0	0.0	1.7721	24.9
8.4	11.6	1.7445	21.7
17.0	22.7	1.7159	18.3
26.0	33.5	1.6865	14.5
35.3	43.9	1.6546	11.7
45.0	53.9	1.6221	8.5
54.9	63.6	1.5874	6.4
65.3	72.9	1.5527	4.6
76.4	82.3	1.5168	3.4
88.1	91.4	1.4806	2.4
100.0	100.0	1.4445	1.7

TABLE 7

Specific Viscosity of the $HNO_3 \cdot 2H_2O - H_2SO_4 \cdot 2H_2O$ System at 20.8°

$HNO_3 \cdot 2H_2O$ % by weight	$HNO_3 \cdot 2H_2O$ Molar %	Specific gravity, $d_4^{20.8}$	Viscosity, centipoises
0.0	0.0	1.6450	12.6
8.6	11.3	1.6196	11.0
17.5	22.3	1.5942	9.5
26.6	32.9	1.5686	8.0
35.6	43.2	1.5430	6.7
45.7	53.3	1.5173	5.7
55.7	63.0	1.4913	4.6
66.1	72.6	1.4653	3.8
76.9	81.8	1.4389	3.1
88.2	91.0	1.4128	2.5
100.0	100.0	1.3860	2.1

method [9], but also by viscosimetry, as shown in the present paper.

We are inclined to regard this substance as nitronium hydropyrosulfate $NO_2[HS_2O_7]$.

3. $N_2O_5 \cdot 4SO_3 \cdot 3H_2O$.

Dode and Pascard, who synthesized this trihydrate in 1949, say nothing about its structure. We, in turn, produced large crystals with this composition synthetically in the same year, 1949. Moreover, in our research on the $HNO_3 - H_2S_2O_7$ liquid system we definitely established the existence of this compound in the liquid state by volumetric analysis and by measuring the viscosity.

The chemical structure of the trihydrate may be that of nitracidium hydropyrosulfate $[H_2NO_3][HS_2O_7]$.

4. $N_2O_5 \cdot 4SO_3 \cdot 5H_2O$.

As we have stated above, this last compound has not been described in the solid state; Hantzsch, Usanovich, and others have assumed its existence in solutions. Our researches have also confirmed the existence of this compound in mixtures of nitric acid and concentrated sulfuric acid. According to our findings, this salt-like compound is hydrolyzed practically completely when the concentration of the sulfuric acid in the mixture falls below 92%.

Hantzsch also considers this hydrate to be hydronitracidium bisulfate $[H_3NO_3][HSO_4]_2$.

5. Our experimental researches indicate that other members of the $N_2O_5 \cdot 4SO_3 \cdot mH_2O$ series than those listed, with an m higher than five, do not exist even in the partially dissociated state.

SUMMARY

1. Several compounds of distinct chemical structure have been found to exist in the liquid ternary system nitrogen pentoxide–sulfur trioxide–water, constituting individual members of a series whose general formula is $N_2O_5 \cdot 4SO_3 \cdot mH_2O$.

2. Some of the members of this series have been isolated in the crystal state.

3. The stability of these compounds decreases as the coefficient m increases, i.e., as the amount of water entering into the compound rises. At values of m in excess of 5 compounds of this type do not exist in the liquid state, even in a partially dissociated state.

4. An endeavor is made to classify the known individual compounds of the $N_2O_5 \cdot 4SO_3 \cdot mH_2O$ series.

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Chair of Inorganic Chemistry,
Ivanovo Institute of Chemical Technology

INVESTIGATION OF THE VOLATILITY OF ALKALI ELEMENTS AT HIGH TEMPERATURE

Vikt. I. Spitsyn, V. I. Shostak, and M. A. Meerov

The information on the volatility of alkali chlorides at high temperature is rather contradictory. Gmelin [1] states that lithium chloride vaporizes at white heat. Hoermann [2] thinks that this salt begins to vaporize at red heat. According to Jaeger [3], lithium chloride vaporizes perceptibly at 960°. This process is extremely rapid above 1080°, the sublimate exhibiting an alkaline reaction when it is wetted with water. The same author states that sodium chloride vaporizes rapidly at 1080°, and very rapidly at 1150°. The reference literature [4] asserts that this compound is perceptibly volatile even at its melting point (i.e., at about 800°). Bunsen [5] notes that potassium chloride is more volatile than sodium chloride. Thürmer [6] believes that potassium chloride vaporizes even in the 200-250° range, evaporation increasing as the temperature rises to dark-red and bright-red heat. According to Jaeger, potassium chloride vaporizes appreciably at 980°, vaporization being very rapid at 1160°. As this author says, the vapor of the salt has an acid reaction, that of the residue dissolved in water being alkaline.

Kirchhoff and Bunsen [7] noted the volatility of rubidium chloride when heated. Jaeger considers that perceptible vaporization of rubidium chloride begins at 950°.

According to Jaeger, cesium chloride begins to vaporize at 925°, the salt evaporating very rapidly at 1000°. Kastler [8] states that cesium chloride is stable in the 300-525° range, beginning to vaporize only at approximately 700°. Marked vaporization is observed at 800°. Kirchhoff and Bunsen assert that cesium chloride is the most volatile of all the chlorides of the alkali elements.

The experimental data in the literature on the vapor pressure of the alkali chlorides usually refer to temperatures above 800-900°. It is not impossible, of course, that the vapor pressure of these compounds is high enough even below these temperatures for perceptible evaporation of samples to occur.

The nature of the gaseous medium may affect the temperature at which vaporization of an alkali chloride sets in, in the opinion of several authors. Jander and Busch [9] found that the vaporization of rubidium chloride was perceptible at 470° in a current of gaseous hydrogen chloride, the corresponding temperature for cesium chloride being 450°. Zintl and Goubeau [10] found potassium chloride to be volatile at 600° in an atmosphere of hydrogen chloride.

The volatility of the alkali chlorides must be taken into account in analytical practice whenever the alkali element is recovered in one way or another from the object of analysis as a chloride and is then brought to constant weight by calcination. For the same reason it is important to regulate the temperature when alkali molybdates, wolframates, niobates, and similar compounds are analyzed by the hydrochlorination method, in which a sample of the substance is calcined in a current of hydrogen chloride, any alkali elements present being converted into chlorides and weighed as a nonvolatile residue.

We have made a thorough study of the temperature at which the perceptible vaporization of chlorides of all the alkali elements sets in in various gaseous media. The experiments were run in a tubular or crucible electric furnace. Temperatures were measured with a platinum-platinum-rhodium thermocouple calibrated at the melting points of zinc and silver. The 0.2-0.3 g samples of the chlorides were placed in porcelain boats, and a current of the given gas was passed through the operating tube at the specified velocity. Heating lasted 1 hour. We also measured the rate of vaporization of the alkali chlorides in air in open platinum crucibles. The temperature was raised in 50° steps in successive runs. The temperature at which vaporization sets in was taken to be that at which a loss of weight of at least 0.0002 g was detected. The initial preparations of the chlorides were analyzed for their chlorine content and found to be satisfactory (Table 1). Spectrum analysis indicated that the cesium chloride contained 0.07% potassium and 0.65% rubidium.

TABLE 1

Analysis of Chlorides of the Alkali Elements

Compound	% Chlorine	
	Found	Calculated
LiCl.....	83.59	83.63
NaCl.....	61.22	61.41
KCl.....	47.34	47.56
RbCl.....	29.38	29.32
CsCl.....	20.98	21.06

TABLE 2

Temperature at which Vaporization of Alkali Chlorides Sets In in Air (Calcination time 1 hour)

Temperature	Change in weight of the chlorides, g				
	LiCl (0.1857 g substance)	NaCl (0.2276 g substance)	KCl (0.2419 g substance)	RbCl (0.2464 g substance)	CsCl (0.2580 g substance)
400°	none	–	–	–	–
450	none	–	–	–	–
500	none	–	–	–	none
550	0.0007	–	–	none	0.0003
600	0.0005	–	none	none	0.0009
650	–	none	0.0003	0.0010	–
700	–	none	0.0012	0.0029	–
750	–	0.0014	–	–	–
Onset of perceptible vapoization	550°	750°	650°	650°	550°

Table 2 gives the results of our determination of the temperature at which the volatilization of the alkali chlorides sets in when they are calcined in air. The tests run in a current of air indicated that perceptible vaporization was observed in the same temperature range, though the loss in an air current exhibited a somewhat greater loss of weight than in calcination in air.

The lowest temperature at which vaporization sets in is exhibited by lithium and cesium chlorides (550°). Lithium chloride exhibits the highest temperature of perceptible vaporization (750°). Volatility increases as we pass from sodium chloride to the chlorides of potassium, rubidium, and cesium. The temperatures we have found for the onset of perceptible vaporization of the alkali chlorides differ considerably from the figures given in the literature, being lower than the earlier figures as a rule. It should be noted that all the alkali chlorides begin to vaporize much (approximately 50-100°) below their melting points (cf. Table 5).

TABLE 3

Temperature at which Alkali Chlorides Begin to Vaporize in a Current of Hydrogen Chloride (10 liters/hour). (Calcination time 1 hour).

Temperature	Change in weight of the chlorides, g				
	LiCl (0.2472 g substance)	NaCl (0.2505 g substance)	KCl (0.2324 g substance)	RbCl (0.2425 g substance)	CsCl (0.2514 g substance)
400°	none	–	–	–	–
450	none	–	–	–	–
500	none	–	–	–	none
550	0.0002	–	–	–	0.0013
600	–	–	–	none	0.0016
650	–	–	none	none	–
700	–	none	0.0002	0.0015	–
750	–	0.0012	0.0015	–	–
Onset of perceptible vaporization	550°	750°	700°	700°	550°

We used the spparatus described by one of the present authors [11] in our study of the volatility of the chlorides in a current of hydrogen chloride. The porcelain boats usually absorb some HCl, and they were therefore first brought to constant weight by calcining them in a current of hydrogen chloride. The test results, given in Table 3, show that the alkali chlorides begin to vaporize perceptibly in an atmosphere of hydrogen chloride at practically the same temperature as in air.

The slight increase in the observed temperature at which vaporization sets in for the potassium and rubidium chlorides is less than 50°, the difference between the temperatures of successive runs. Thus, we are unable to confirm the Jander and Busch findings that the vaporization temperature of rubidium and cesium chlorides drops appreciably in an atmosphere of hydrogen chloride.

TABLE 4

Temperature at which Vaporization of Alkali Chlorides Sets In in a Current of Steam (6 g/hour)

Temperature	Change in weight of the chlorides, g				
	LiCl (0.2776 g substance)	NaCl (0.2256 g substance)	KCl (0.2076 g substance)	RbCl (0.2195 g substance)	CsCl (0.2113 g substance)
400°	none	—	—	—	—
450	none	—	—	—	none
500	0.0001	—	—	—	0.0001
550	0.0025	—	—	none	0.0008
600	0.0035	—	none	0.0006	0.0023*
650	—	none	0.0004	—	—
700	—	none	0.0019	—	—
750	—	0.0013	—	—	—
Onset of perceptible vaporization	550°	750°	650°	600°	550°

* The sample weighed 0.2124 g in this run initially.

Our temperature for the onset of vaporization of lithium chloride in a current of HCl agrees with our previous results as found in analyzing lithium wolframates [12].

Alkali chlorides were calcined in a current of steam as follows. A certain quantity of water was heated in a small conical flask, which was sealed with a stopper through which an outlet tube was passed. The steam passed into an operating quartz tube placed within an electric furnace and containing a boat with a sample of the chloride. The inlet section of the quartz tube was heated externally to 150–200° by means of a Bunsen burner to prevent condensation of the steam. The operating tube was connected to a glass collector flask fitted with a reflux condenser. Part of the chloride that vaporized at the respective temperature conditions settled on the colder wall of the quartz tube, the rest entering the collector together with the condensate. In view of the hygroscopicity of lithium chloride, the sample of this substance was heated to 400° for 30 minutes in a current of anhydrous air after the steam run.

TABLE 5

Comparison of the Melting Points and the Onset of Perceptible Vaporization of Alkali Chlorides in Various Gaseous Media

Alkali Chloride	M.p.	Onset of perceptible vaporization, (°)			Difference between the melting points and the temperatures at which vaporization of the alkali chlorides begins in air (round figures) (°)
		In air	In a current of HCl	In a current of steam	
LiCl....	605°	550°	550°	550°	50°
NaCl...	800	750	750	750	50
KCl....	770	650	700	650	120
RbCl...	726	650	700	600	75
CsCl...	646	550	550	550	100

Research has established that the vaporization of most of the alkali chlorides in a current of steam begins in the same temperature range as in the analogous calcination tests in the air. Only in the case of rubidium chloride is the temperature at which vaporization sets in lowered by 50° (Table 4).

It should be again emphasized that for most of the alkali chlorides (LiCl, NaCl, and CsCl) the temperatures at which vaporization begins is the same in the media tested. In an atmosphere of HCl potassium chloride begins to vaporize at a temperature that is 50° higher than in air or in a current of steam. In a current of HCl rubidium chloride vaporizes at a temperature that is 50° higher than in air, the respective temperature in steam being 50° lower than in air. Inasmuch as the experiments were run using temperature intervals of 50°, we may conclude that the nature of the gaseous medium has no substantial effect upon the temperature at which the alkali chlorides begin to vaporize. As Table 5 also indicates, the vaporization of the alkali chlorides begins to be perceptible at temperatures that are 50 to 120° below the melting points of the compounds in question. Lithium and sodium chlorides vaporize at temperatures closer to their melting points. The difference between the onset of vaporization and the melting point is much greater (some 75 to 120°) in the cases of potassium, rubidium, and cesium chlorides. The lowest temperatures at which vaporization sets in (550°) are found for lithium and cesium chlorides, these temperatures being nearly identical. The highest temperature at which vaporization begins is found in sodium chloride

(750°). The volatility of potassium and rubidium chlorides lies between that of sodium and cesium chlorides.

It may be postulated that the most volatile alkali chlorides are those in which the chemical bond is least typically ionic. Owing to the substantial polarizing action of the lithium ion, lithium chloride is one such chloride. Sodium chloride is more ionic, because of the increase in the cation's radius and its lesser polarizing effect, and, as we know, it has the highest melting point of all the alkali chlorides as well as the highest temperature for the onset of vaporization. The gradual increase in volatility as we pass to the chlorides of potassium, rubidium, and cesium may be caused by the deforming action of the chlorine ion upon the ion of the alkaline element, this action increasing with the increase in the radius of the latter. The appearance of a perceptible vapor pressure of the alkali chlorides at temperatures in the vicinity of their melting points forces us to conclude that the bond becomes less ionic and more polar when these substances are melted.

The results of the tests we have described afford some conclusions regarding the relative velocity of vaporization of the alkali chlorides in various gaseous media at temperatures in the vicinity of the point at which perceptible vaporization of these compounds begins. The loss of weight in a current of steam is, as a rule, several times greater than the loss of weight observed during calcining in air or in a current of hydrogen chloride (Table 6). An exception to this is sodium chloride, which exhibits an approximately equal loss of weight in all three of the media studied.

TABLE 6

Rate of Vaporization of Chlorides of the Alkali Elements at Temperatures in the Vicinity of the Onset of Perceptible Vaporization (Calcination time 1 hour. Samples weighing about 0.25 g).

Chloride	Temp. of run	% loss of weight		
		In air	In a current of HCl (10 l/hr)	In a current of steam (6 g/hr)
LiCl.....	550°	0.48	0.08	0.90
NaCl....	750	0.62	0.48	0.58
KCl.....	700	0.49	0.09	0.92
RbCl....	600	none	none	0.27
CsCl....	600	0.35	0.64	1.08

TABLE 7

Analysis of the Products of the Sublimation of Lithium and Cesium Chlorides in a Current of Steam (Heating for 30 min to 800°. Steam flow rate: 18 g/hr).

Chloride	% Chlorine in initial chloride	% Chlorine in the sublimation products		
		Calcination residue	Sublimate	Dry residue of condensate
LiCl....	83.59	82.96	83.12	81.47 ±2%
CsCl...	20.98	20.97	21.00	21.72 ±2%

Vikt. I. Spitsyn and V.I.Shostak [13] recently found that the rate of vaporization of normal alkali sulfates at high temperatures is likewise increased considerably in the presence of steam. This phenomenon is, therefore, apparently observable in many compounds.

Nothing conclusive can be said regarding the effect of hydrogen chloride. According to the data in Table 6, lithium, sodium, potassium, and rubidium chlorides exhibit a more or less significant decrease in volatility in hydrogen chloride, as compared to calcination in air, this decrease being least perceptible in sodium chloride. In the case of cesium chloride the loss of weight in a current of hydrogen chloride is greater than in air, but less than in a current of steam.

The problem of how the nature of the gaseous medium affects the rate of vaporization of various substances requires further study. In so far as steam is concerned, however, it may be assumed that its singular behavior is due to the same causes that are responsible for the action of liquid water upon substances dissolved in it. The rate at which the alkali chlorides vaporize increases with rising temperature and with an increase in the steam flow rate.

Analysis of the calcination residue, the sublimate in the tube, and the condensate in the receiver indicated that these products exhibited a neutral reaction in solution in the case of all the alkali chlorides. The sublimate and the calcination residue were analyzed for chlorine in the case of the lithium and cesium chlorides (Table 7). The samples of these salts (weighing about 0.1 g) were heated for 30 minutes to 800°. The sublimate weighed 0.040 to 0.045 g. The condensate contained 0.002-0.003 g of the vaporized chloride, as indicated by evaporating the condensate to dryness. The products were analyzed by the Mohr method. It was found that there was no appreciable difference between the composition of the sublimate and that of the initial substance or of the calcination residue. The analysis of the chloride in the condensate was done as a check. In view of the small percentages of the substance analyzed, the possible errors in the determination of the chlorine amounted to ± 2% in this case. Thus, the rapid

vaporization of alkali chlorides in a current of steam at the comparatively low temperatures investigated involves no perceptible hydrolysis.

Cabot's findings on the hydrolysis of sodium chloride by superheated steam [14] evidently refer to a higher temperature. Sen, Sen-Gupta, and Das-Gupta [15] have observed only slight decomposition of sodium chloride by steam at 500-810°. Guthrie and Nance [16] have observed slight hydrolysis of lithium chloride in the 430-530° range. Briner and Roth [17], on the other hand, have found that alkali chlorides are appreciably decomposed by steam, forming hydrochloric acid, at 550° (decomposition of 0.5 to 1.2% in one hour). The extent of hydrolysis increased to 14-33% at 900°, depending upon the nature of the compound tested. The cited paper does not say how the vaporization of the alkali chlorides, which becomes quite noticeable at temperatures in excess of 550-750°, was taken into account. There is no doubt that a high percentage of the chlorine was eliminated from the sample by the direct vaporization of the chloride.

Our experimental findings indicate that steam causes no appreciable decomposition of alkali chlorides at temperatures in the vicinity of the latter's melting points. In this instance, vaporization is evidently more rapid than hydrolysis. These phenomena are of geochemical interest. The action of superheated steam upon deep rocks whose temperature is sufficiently high ought to promote the vaporization of alkali chlorides from these rocks and the migration of these compounds closer to the earth's surface.

SUMMARY

1. A study has been made of the temperature conditions under which perceptible vaporization of the alkali chlorides occurs in various gaseous media (air, hydrogen chloride, and steam).

2. In air vaporization has been observed to set in at the following temperatures:

LiCl	NaCl	KCl	RbCl	CsCl
550°	750°	650°	650°	550°

3. In a current of hydrogen chloride or of steam vaporization of these compounds has been found to set in at the same temperatures (±50°).

4. The alkali chlorides exhibit perceptible volatility at temperatures that are 50-120° below their respective melting points.

5. It has been found that alkali chlorides vaporize at a much higher rate in a current of steam than in air or in hydrogen chloride. This process is not accompanied by hydrolysis phenomena at the test temeratures employed (550-800°).

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Received October 12, 1950 Laboratory of Inorganic Chemistry, Moscow State University

THE MECHANISM OF THE CATALYTIC TRANSFORMATIONS OF HYDROCARBONS OVER A VANADIUM CATALYST

VII. THE COMPARATIVE BEHAVIOR OF BINARY MIXTURES OF HEPTANE, HEPTENE AND TOLUENE

A. F. Plate and G. A. Tarasova

In our earlier researches on the behavior of individual heptane, heptene-1, and heptene-3 in the presence of a vanadium catalyst [1] we have shown that the aromatization reaction is accompanied by a reversible dehydrogenation–hydrogenation of heptane $\rightleftarrows$ heptene and we suggested that heptene is not the inevitable intermediate product of the aromatization of heptane. A study of the effect of the principal reaction products of the aromatization of heptane–heptene and toluene upon the aromatization of the heptane constituted an extension of our investigation of the role of heptene in the aromatization of heptane. With this in view, we aromatized binary mixtures consisting of heptane, heptene-1, and toluene. They are not many papers in the literature upon the aromatization of hydrocarbon mixtures of definite composition.

The aromatization of heptane-heptene mixtures containing 10% to 80% of heptene was investigated by Green [2]. According to that author, the percentage of toluene in the catalyzate decreases as the percentage of heptene in the mixture is raised. These findings are contradicted, however, by numerous observations that heptene is aromatized more readily than heptane. The conclusions reached by Green apparently depend upon the specific conditions under which his experiments were run: the use of a cracking catalyst (2% MoO_3 on Al_2O_3) and operation at high temperature (550°). Taylor and Fehrer [3] aromatized a mixture of heptane and 15% of heptene with a chrome catalyst and found that somewhat more toluene was produced from such a mixture than from pure heptane under the same conditions. We find the fullest data on the aromatization of hydrocarbon mixtures in R. D. Obolentsev and Yu. N. Usov [4], who explored the behavior of a series of alkane-alkene mixtures at 485° over a chrome contact catalyst. In particular, they investigated the aromatization of two mixtures containing heptane and 30 and 50%, respectively, of heptene-1, as well as the aromatization of each of these individual hydrocarbons. The authors showed that there is a direct relationship between the percentage of heptene in the mixture and the amount of toluene produced and concluded that "the mixture components undergo conversion independently of each other, as it were." Nor has much work been done upon the effect of adding toluene upon the aromatization of heptane. Oblad, Marschner, and Heard [5] aromatized a heptane mixture containing 25% of toluene at 482° with chromic oxide on alumina. The authors concluded that heptane mixed with toluene is aromatized in proportion to the concentration of heptane in the mixture. Green [2] aromatized several mixtures, containing 24 to 92% of toluene in addition to heptane. Although aromatization was accompanied by thermal cracking, the author concluded that the heptane is converted into toluene even when the initial mixture contains an appreciable percentage of toluene. We know of no papers in the literature on the aromatization of heptene in the presence of toluene.

The present paper is a report on the behavior of mixtures of heptane–heptene, heptane–toluene, and heptene–toluene under identical conditions of temperature, rate of flow, and length of run in the presence of the same sample of vanadium catalyst. Experiments with heptane–heptene mixtures have shown that the percentage of toluene in the catalyzate rises with an increase in the percentage of heptene in the mixture. This relationship is represented by a straight line like the one previously found by Obolentsev and Usov for a series of alkane-alkene mixtures in the presence of a chromic catalyst. We can therefore say that in a mixture of heptane and heptene each hydrocarbon is aromatized in proportion to its concentration. This conclusion is borne out by an experiment involving the aromatization of a mixture of heptane and 2-methylbutene-2 under the same conditions. We thought it would be interesting to aromatize heptane in the presence of an alkene that could not form a six-membered ring. It was found that the yield of toluene from such a mixture was the same as its yield from heptane alone, or, in other words, heptane reacts in this mixture in proportion to its concentration. Aromatization of heptane-toluene mixtures indicated that the amount of newly formed toluene was directly

proportional to the percentage of heptane in the mixtures, whereas when heptene-toluene mixtures were aromatized, the amount of toluene formed was not a linear function of the percentage of heptene in the original mixture, the share of the reacting heptene rising sharply as its percentage in the mixture was decreased. Hence, heptane behaves differently in a mixture with toluene than heptene does, although each of them is aromatized in proportion to its concentration when mixed together. These contradictory conclusions cannot be reconciled if we assume that heptane and heptene are aromatized at the same active centers. But if we assume that these hydrocarbons are aromatized at different centers, the facts we ascertained are not mutually contradictory. Such an assumption appears to be highly probable in view of the complicated nature of the surface of a mixed oxide catalyst.

EXPERIMENTAL

The catalyst consisted of vanadium oxide deposited on alumina [1]. The catalyst was regenerated by air and then reduced with hydrogen before each series of tests. It exhibited no change of activity during this procedure.

Apparatus and operational procedure. The tests were made in the circulating system described by us previously. In this research we chose another method of liquid supply. Instead of an automatic buret we used a graduated cylinder with a piston [6], which was lowered evenly by the action of a motor, thus ensuring uniformity of the liquid supply. The temperature was 480° in all the tests. The volumetric rate was 0.5 in every run. The operational procedure was as follows. Each series of tests was run during a single day without turning off the furnace. A mixture of a certain composition was passed through for 30 minutes, after which hydrogen was blown through the catalyst (for 35-40 minutes) to drive off the catalyzate. Then a mixture of a different composition was run through, and so on. The pure components of the mixture was run through in the same series of tests, as a check on the activity of the catalyst. The percentage of unsaturated hydrocarbons was determined, as usual, by the bromine number method [8]. We employed the methods of specific and relative dispersions to determine the percentage of toluene [7]. The method of relative dispersions was first tested with artificial heptane-toluene and heptene-toluene mixtures.

Aromatization of heptane-heptene mixtures. In this series of tests we investigated the behavior of five mixtures containing 5 to 30% of heptene-1, as well as the behavior of pure heptene and heptane. The results of these tests are listed in Table 1 and shown graphically in Fig. 1. In this fiture Curve I represents the percentage of toluene in the catalyzate; it is a straight line, as we see. Curve II indicates the behavior of the

TABLE 1

Test No.	Original mixture					Catalyzate				
	Composition, mol. %		n_D^{20}	Bromine number	Per cent unsaturated	n_D^{20}	Bromine number	Per cent unsaturated		Per cent aromatics
	Heptane	Heptene						By weight of the catalyzate	± Δ %	
31[1]	100	0	1.3875	0.0	0.0	1.3923	11.9	7.5	+ 7.5	6.0
31[2]	95	5	1.3880	7.5	4.7	1.3942	13.9	8.7	+ 3.7	8.0
31[3]	90	10	1.3887	15.9	10.0	1.3964	15.6	9.7	− 0.3	9.0
31[4]	50	50	1.3933	79.3	49.1	1.4089	36.8	23.0	−26.0	24.0
31[5]	25	75	1.3964	121.0	74.5	1.4190	57.9	35.6	−38.9	30.5
31[6]	10	90	1.3983	144.9	88.9	1.4261	72.2	44.3	−44.6	37.0
31[7]	0	100	1.3997	(163.3)[1)]	100.	1.4297	86.7	53.1	−46.9	40.5

heptene in this mixture, based on the change in the bromine numbers of the catalyzate. When the mixture contains less than 10% of heptene, the percentage of unsaturated compounds in the catalyzate increases (cf Table 1, Col. 10 and the left-hand branch of Curve II, Fig. 1). When the mixture contains more than 10% of heptene, its percentage in the catalyzate drops (cf Table 1, Col. 10, and the right-hand branch of Curve II, Fig. 1).

Aromatization of a mixture of heptane and 2-methylbutene-2. We investigated the behavior of a single mixture, containing 22.7 mol.% of 2-methylbutene-2. The mixture was run through at 480° for five hours. The catalyzate was identified and then fractionated into a column with an efficiency of 40 theoretical plates. The analysis of the catalyzate and of its fractions is given in Table 2.

As the table indicates, the catalyzate was separated into four fractions, which represented the following

[1)] Calculated.

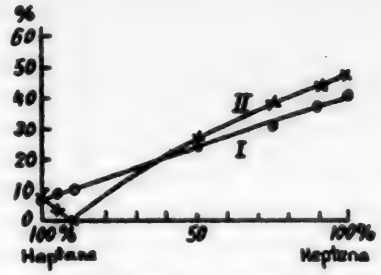

Fig. 1. Aromatization of heptane-heptene mixtures.

I - Per cent toluene in the catalyzates; II - change in the percentage of heptane in the catalyzates.

constituents: I—isopentene; II—heptene-heptane; III—heptane; and IV—heptane-toluene. When we compute the percentage of toluene in that portion of the catalyzate corresponding to the last three fractions, we get a figure of 8.9%. Comparing these results with Tests 31[1] (Table 1) and 34[6] (Table 3), in which the catalyzates produced by aromatizing heptane at the same temperature contained 6.0 and 8.5% of toluene, respectively, we may conclude that when mixed with 2-methylbutene-2, heptane is aromatized in proportion to its concentration. The heptene yield, based on Fractions II, III, and IV, was 7.1%, which also agrees with the results of Tests 31[1] and 34[6], in which the percentages of unsaturated compounds in the catalyzates totaled 7.5 and 7.2% respectively. When the heptenes were aromatized, we noted that they were partially hydrogenated [1]. In this instance of the aromatization of a mixture of heptane and 2-methylbutene, we again observed that the alkene was hydrogenated. The isopentene fraction contained 15% of saturated hydrocarbons.

The aromatization of heptane-toluene mixtures was explored in five mixtures, containing from 10 to 90% of toluene. The composition of the original mixtures and the test results are given in Table 3 and shown graphically in Fig. 2. Curve I indicates the percentage of newly formed toluene, while Curve II

TABLE 2

Fractionation and Analysis of the Fractions of the Catalyzate Produced from a Mixture of Heptane and 2-Methylbutene-2

Fraction	Boiling point at 760 mm, °C	Weight, grams	Weight, %	n_D^{20}	d_4^{20}	Bromine number	% Unsaturated		% Aromatics	
							Of the fraction	Of the catalyzate	Of the fraction	Of the catalyzate
Entire catalyzate		29.5	100	1.3912	0.6875	31.4	—	18.8	—	6.7
I	27.4-38.0	3.2	10.8	—	—	193.9	85.1	9.2	—	—
II	38.0-97.5	2.8	9.5	—	—	57.5	35.3	3.4	—	—
III	97.5-98.5	20.0	67.7	1.3912	0.6890	6.5	4.1	2.8	8.7	5.9
IV[1]	98.5-101.0	3.3	11.1	1.4015	0.7070	3.0	1.8	0.2	20.0	2.2
	Residue	0.2	0.9	—	—	—	—	—	—	—
	Losses	None	—	—	—	—	—	—	—	—

TABLE 3

Aromatization of Heptane-Toluene Mixtures

Test No.	Original mixture			Catalyzate						
	Per cent by weight		n_D^{20}	n_D^{20}	Bromine number	% unsaturated, by weight		% aromatics, by weight		
	Heptane	Toluene				Of catalyzate	Of initial heptane	Of catalyzate	Δ, based on weight of catalyzate	Δ, based on initial heptane
34[6]	100	0	1.3875	1.3956	11.7	7.2	7.2	8.5	8.5	8.5
34[2]	90.0	10.0	1.3960	1.3960	14.6	9.0	10.0	16.0	6.0	6.7
34[1]	77.0	23.0	1.4075	1.4139	11.2	6.8	8.8	30.0	7.0	9.1
34[3]	49.5	49.5	1.4325	1.4363	8.9	5.3	10.7	53.0	3.5	7.1
34[5]	26.5	73.5	1.4606	1.4646	3.3	1.9	7.2	76.3	2.8	10.6
34[4]	10.0	90.0	1.4805	1.4803	1.8	1.0	10.0	89.0	(1)	(10)

[1] Distilled from a Würtz flask.

TABLE 4

Aromatization of Heptene-Toluene Mixtures

Test No.	Original mixture, % by weight: Toluene	Heptene	n_D^{20}	Catalyzate: n_D^{20}	Bromine number	% unsaturated by weight: of entire catalyzate	± Δ	% aromatics by weight: of entire catalyzate	Δ, Based on weight of catalyzate	Δ, Based on original heptane
32[8]	0	100	1.3997	1.4245	112.0	67.2	− 32.8	38.3	38.3	38.3
33[7]	0	100	1.3997	1.4277	105.0	62.8	− 37.2	36.0	36.0	36.0
32[6]	11.2	88.8	1.4078	1.4332	94.1	55.5	− 33.3	41.3	30.1	33.9
33[3]				1.4370	87.4	52.0	− 36.8	46.0	34.8	39.2
32[7]	21.5	78.5	1.4163	1.4400	85.6	50.8	− 27.7	48.0	26.5	33.8
33[6]				1.4456	72.5	42.9	− 35.6	54.7	33.2	42.3
32[5]	30.8	69.2	1.4232	1.4494	68.6	40.9	− 28.3	58.7	27.9	40.3
32[3]	50.9	49.1	1.4411	1.4649	43.8	25.6	− 23.5	72.7	21.8	44.4
33[1]				1.4638	43.7	25.6	− 23.5	72.0	21.1	43.0
33[2]				1.4625	46.6	27.3	− 21.8	71.5	20.6	42.0
33[4]	76.2	23.8	1.4674	1.4813	19.5	11.3	− 12.5	88.0	11.8	49.6
32[1]	90.2	9.8	1.4838	1.4919	5.6	3.1	− 6.7	96.5	6.3	64.3
32[2]				1.4925	4.6	2.6	− 7.2	97.5	7.3	74.5
33[4]	94.7	5.3	1.4897	1.4924	6.5	3.8	− 1.5	97.2	2.5	47.2
33[5]	100	0	1.4965	1.4951	1.6	0.9	+ 0.9	99.4	—	—

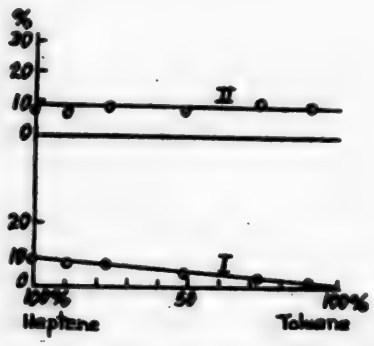

Fig. 2. Aromatization of heptane-toluene mixtures.

I - Percentage of toluene formed; II - toluene yield, based on initial percentage of heptane.

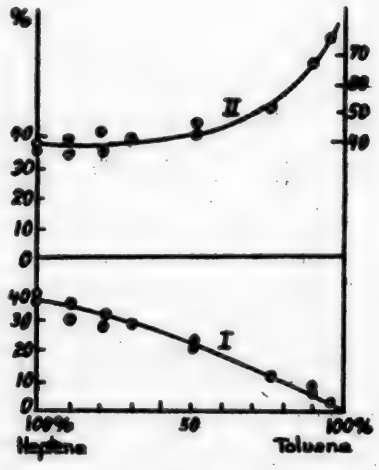

Fig. 3. Aromatization of heptene-toluene mixtures.

I - Per cent of toluene produced; II - toluene yield, based on the percentage of the original heptene.

gives the toluene yield, based on the initial percentage of heptane. The results of these tests indicated that the percentage of newly formed toluene is directly proportional to the percentage of heptane in the mixture, while the percentage of toluene, based on the heptane in the mixture remains constant.

Aromatization of heptene-toluene mixtures. Seven mixtures, containing from 11 to 95% toluene, were

tested. We ran two sets of tests, the results being fairly well reproducible. Moreover, in both sets we aromatized pure heptane, while in one set we passed toluene over the catalyst.

The test results are listed in Table 4 and shown graphically in Fig. 3. Curve 1 represents the percentages of reacted heptene and toluene produced, the respective points coinciding, thus constituting a single curve. As the graph indicates, this function is expressed by a slightly convex curve. Curve II in Fig. 3 represents the toluene yield as a function of the heptene concentration in the mixture. To judge from this curve, the smaller the percentage of heptene in the mixture, the larger the proportion of the heptene that reacts. Inasmuch as the graphs showing the results of all the three binary mixtures have been plotted in the following coordinates: mixture composition versus percentage of toluene produced, the shapes of these curves indicate how these hydrocarbons displace one another. The straight line in Fig. 2, which represents the aromatization of heptane - toluene mixtures, shows that heptane and toluene are adsorbed at the surface of the catalyst in proportion to their concentrations. Heptane and heptene are adsorbed in the same manner (Fig. 1), while heptene is better adsorbed than toluene (upper curve in Fig. 3). This discrepancy between the behavior of heptane and heptene may be due to the fact that heptane and heptene are aromatized at different active centers in an oxide catalyst. In this case, it would seem that heptene is not necessarily an intermediate product in the aromatization of heptane.

SUMMARY

1. A study has been made of the aromatization of heptane-heptene mixtures at 480° over a catalyst consisting of vanadium oxide deposited upon alumina; it has been found that the percentage of toluene formed is directly proportional to the percentage of heptene in the mixture.

2. It has been shown that when the percentage of heptene in the mixture is below 5%, its percentage in the catalyzate increases, when its percentage is 10%, the percentage in the catalyzate remains constant, and when its percentage exceeds 10%, the percentage of unsaturated compounds in the catalyzate falls below the initial percentage.

2. A mixture of heptane and 2-methylbutene-2 (22.7 mol.%) has been aromatized at 480°. It has been found that the heptane in the mixture yields toluene and heptene in proportion to its concentration. Under these conditions part of the isopentene is hydrogenated to isopentane.

3. A study has been made of the effect of adding toluene (ranging from 10 to 90%) upon the aromatization of heptane at 480°. It has been found that the percentage of newly produced toluene is directly proportional to the percentage of heptane in the mixture; correspondingly, the toluene yield remains constant, based upon the percentage of the initial heptane.

4. A study has been made of the effect of adding toluene (ranging from 11.8% to 95.0%) upon the aromatization of heptene at 480°. It has been shown that the toluene yield, based upon the initial heptene, rises as the concentration of heptene in the mixture falls.

5. Comparison of the results of aromatization of the three binary mixtures: heptane-heptene, heptane-toluene, and heptene-toluene, seems to indicate that heptane and heptene are aromatized at different active centers of the catalyst.

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Institute of Organic Chemistry,
U.S.S.R. Academy of Sciences

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SYNTHESIS OF HYDROCARBONS BY THE ACTION OF HEXACHLOROETHANE UPON ORGANOMAGNESIUM COMPOUNDS

V. V. Korshak and T. D. Kozarenko

In his research into the reaction of hexachloroethane with organomagnesium compounds with the objective of synthesizing hexaaryl and hexaalkyl ethanes, one of the present authors [1] discovered that the following reaction:

$$2RMgX + C_2Cl_6 \rightarrow R \cdot R + C_2Cl_4 + 2MgClX.$$

took place, instead of the expected ethanes being synthesized.

This principal reaction was paralleled by reduction of the hexachloroethane, so that we secured, in addition to tetrachloroethylene, lower chlorine derivatives of ethane: pentachloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, and trichloroethane.

Organomagnesium compounds prepared from bromobenzene, p-bromotoluene, α-bromonaphthalene, and ethyl bromide were used in our investigation of this reaction. The first three compounds yielded diphenyl, ditolyl, and dinaphthyl, respectively. Ethylmagnesium bromide yielded ethane and ethylene.

Inasmuch as this reaction might be of interest as a new method of synthesizing hydrocarbons, we have returned to it in the present paper, setting as our objective the determination of the conditions that might ensure adequately high yields of the hydrocarbons.

To do this, we investigated the reaction of hexachloroethane with the organomagnesium compounds prepared from bromobenzene, α-bromonaphthalene, benzyl chloride, ethyl bromide, and methyl iodide. We ran a series of tests with each of these substances, in which we varied the reaction temperature, the concentration of the reagents, and the process time. In addition, we investigated the influence of the nature of the solvent, testing diethyl ether, dibutyl ether, diisoamyl ether, and mixtures of the latter two with diethyl ether as media.

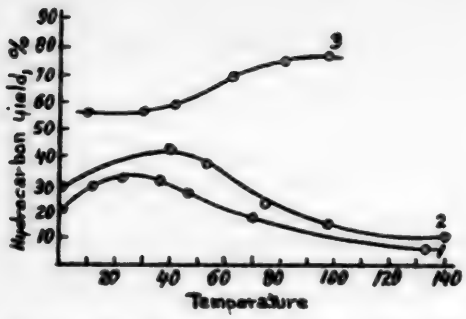
Our investigations indicated that this method made it possible to secure 33% to 79% of the theoretical yields of hydrocarbons, based on the halogen derivative employed in the reaction.

It is advisable to produce the organomagnesium compound in diethyl ether and then to add the hexachloroethane, dissolved in dibutyl or diethyl ether. Then part of the diethyl ether is driven off to fix the boiling point of the mixture at the optimum value. The optimum reaction temperature, producing the highest yield of the hydrocarbon, is 97° for benzyl chloride, 40° for bromonaphthalene, and 22° for bromobenzene. The yields drop off sharply above and below these temperatures, as may be seen from the figure.

When methylmagnesium iodide is reacted with hexachloroethane, it yields ethane and methane (39% and 61% respectively). Ethylmagnesium bromide yields a gas that consists chiefly of ethylene (77.8%) and contains 14.3% of ethane and 7.9% of butane.

It is worthy of note that the composition of this gas is close to the composition of the gas produced by Carothers [2] in the thermal decomposition of ethylsodium and of a coordination compound of the latter with diethylzinc (84.3% ethylene, 14.9% ethane, and 0.3% butane).

This may be regarded as confirming the idea we advanced earlier [1] to the effect that this reaction involves a stage in which free radicals are formed, so that the result depends upon the properties of the free radical. With aromatic radicals dimers are produced, whereas in the case of the unstable ethyl radical, which tends to split off hydrogen, there is only very little dimerization, the principal reactions being disproportionation ($2C_2H_5 = C_2H_4 + C_2H_6$) and the splitting off of hydrogen ($C_2H_5 = C_2H_4 + H$).



Hydrocarbon yield as a function of temperature. 1 - Diphenyl; 2 - dinaphthyl; 3 - dibenzyl.

Another factor serving to confirm the presence of free radicals in this transformation is the fact that a solution of an organomagnesium compound to which hexachloroethane has been added proves to be able to initiate the polymerization of styrene more vigorously than a solution of magnesium-ethyl bromide containing no hexachloroethane. As we know, the initiated polymerization of styrene and other polymerizable monomers sets in under the action of free radicals, produced by the decomposition of benzoyl peroxide or similar substances that can break down to yield free radicals [3]. It is therefore apparent that the solution of an organomagnesium compound gives off free radicals in the presence of hexachloroethane, that initiate the polymerization of styrene.

EXPERIMENTAL

Preparation of dibenzyl. Five grams of magnesium shavings and 70 ml of absolute ether were placed in a 500-ml four-necked flask fitted with a stirrer, a reflux condenser, a dropping funnel, and a thermometer. Then 30 g of benzyl chloride was added a drop at a time to the flask contents, with constant stirring (see Footnote 1). When nearly all the magnesium had dissolved, 25 g of hexachloroethane, dissolved in 70 ml of anhydrous n-dibutyl ether was added to the resultant organomagnesium compound (see Footnote 2). Part of the diethyl ether was driven off (via a straight condenser) to raise the boiling point of the reaction mixture to 80-90°. The mixture was kept at this temperature for 4 hours, after which the resultant coordination compound was decomposed with water and dilute sulfuric acid. The ether layer was dried over calcined calcium chloride and then fractionated in vacuo. The yield of dibenzyl with an m.p. of 51.2° was 16.6 g or 87% of the theoretical.

Other hydrocarbons may be produced in the same manner.

Footnotes. 1. When bromobenzene and α-bromonaphthalene are used, a crystal of iodine is added to the ether to shorten the induction period. 2. Whenever the temperature must not exceed +45°, it is advisable to substitute diethyl ether for the dibutyl ether.

SUMMARY

1. The reaction of hexachloroethane with organomagnesium compounds has been explored.

2. It has been shown that this reaction results in the formation of hydrocarbons that are dimers of the radicals making up the organomagnesium compound in the case of aromatic radicals and the methyl radical.

3. It has been shown that in the case of ethylmagnesium bromide only little butane is formed, the principal product being ethylene with some ethane.

4. It has been shown that organomagnesium compounds are initiators of the polymerization of styrene, especially when hexachloroethane is present.

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Institute of Organic Chemistry,
U.S.S.R. Academy of Sciences

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THE ADDITION OF α-HALOGEN ETHERS OF THE $CH_3CHCl-O-R$ TYPE TO BUTADIENE

A. N. Pudovik

Study of the order and mechanism in which halogens, halogen acids, hypohalogenous acids and their esters, and various halogenous organic compounds are added to butadiene is of considerable interest in organic chemistry. Not so long ago it was generally assumed, on the basis of the work of Thiele and other chemists, that the halogens and halogen acids are added to butadiene chiefly, or exclusively, at the 1, 4 position, Thiele's notions, based on the assumption of the existence of partial valencies in carbon atoms, being used to explain the addition mechanism. Subsequently, with the development of electronic concepts in organic chemistry, a series of electronic schemas were proposed to explain the mechanism of addition; the most widespread acceptance being accorded to Ingold's and Burton's ionic mechanism (1928) [1]. More thoroughgoing investigation of the reactions involved in the addition of various reagents to butadiene, carried out in the past two decades, however, have shown that the findings of the earlier researches on the order in which addition occurred contained substantial errors in most instances, while in some cases they were wholly wrong. This is due to the fact that these researches either wholly ignored or else paid too little attention to the allyl rearrangements of the addition products (which are typical allylic isomers) that occur during the reaction, separation, and refining. More careful experiments, in which various precautions were taken to exclude or to reduce to a minimum the thermal isomerization of the addition products during the reaction and during the processing of the reaction mixture, have indicated that the halogens chlorine and bromine [2], and the halogen acids [3], are added to butadiene principally at the 1,2 position.

The papers by A.A. Petrov [4] and by B. A. Arbuzov and V.M. Zoroastrova [5] have shown that hypohalogenous acids and their esters are likewise chiefly added, and in some instances exclusively added, at the 1,2 position.

The problem of the order of addition of α-halogen ethers to butadiene had received hardly any attention in the literature prior to our recent papers. We used the addition of several α-halogen ethers of the general type of $CH_2Cl-O-R$ to show that it is the catalytic isomerization, rather than the thermal isomerization, of the chloroallylic isomers during the reaction processes occurring in the presence of zinc chloride or halides of other metals that is highly important in determining the order of addition of the alpha halogen ethers. This new and important factor was unknown prior to that time and hence could not be allowed for in earlier researches.

Allowing for catalytic isomerization, we found that 73-75% of chloromethyl ether [6] is added to butadiene at the 1,2 position, 25-27% being added at the 1,4 position, while 65-75% of chloromethyl ethyl and chloromethyl butyl ethers are added to butadiene at the 1,2 position, with 25-35% being added at the 1,4 position. This proved that the alpha halogen ethers, like the halogens, the halogen acids and the esters of hypohalogenous acids, are added to butadiene at the 1,2 position much more than at the 1,4 position.

In view of the theoretical interest of our results, we resolved to make a study of the addition of halogen ethers of the $CH_3CHCl-O-R$ general type to butadiene in the present research by way of an extension and expansion of our inaugurated researches. We prepared the halogen ethers in the usual manner, by reacting hydrogen chloride with a mixture of acetaldehyde and the corresponding alcohol, the addition to butadiene being effected by the procedure described in our preceding papers. [1)]

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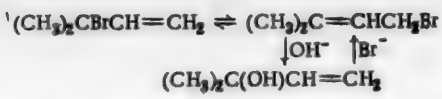
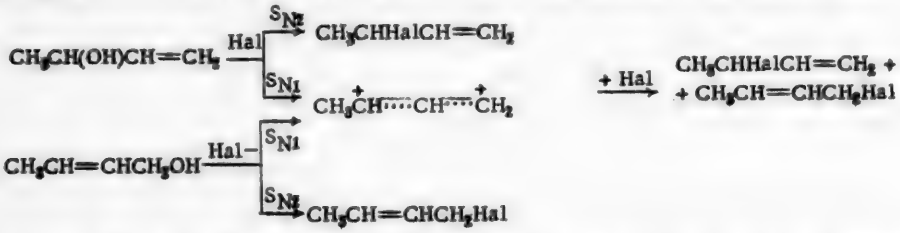
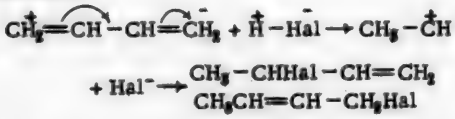
1) After our research had been completed there appeared a paper by Emerson, Deebel, and Longley [8], in which the authors describe the addition of several alpha halogen ethers to butadiene, referring to the paper by Straus and Thiele and to one of our papers. Many of the reactions carried out by the American authors have been described somewhat earlier in one of our reports [7]. They also secured the addition products of some alpha chloroethyl alkyl ethers to butadiene.



cannot be regarded as sufficiently convincing in our opinion. The results of reactions involving the addition of halogen derivatives to butadiene must be compared with reactions of the following type:



in which there is a direct analogy with addition reactions of butadiene, rather than with the examples cited above, in which a kinetic factor is actually manifest but which exhibit no such direct analogy with butadiene addition reactions. In the halohydrination of butenyl alcohols, the reaction is largely monomolecular [13], yielding the same intermediate form of the carbonium ion as must be produced in the step-by-step addition of, say, hydrogen chloride to butadiene:



The results of these two reactions are wholly different, however. In the case of addition, it is the secondary chloride that is chiefly produced (75% 1,2 addition), while it is a primary halide that is formed in monomolecular substitution. No appreciable kinetic factor is observed in the latter reactions, the ratio of the isomeric halides being close to that in the equilibrium mixture, readily attained in their thermal or catalytic isomerization. In several of our preceding papers, we have expressed the opinion, which we continue to maintain in the present paper, that the addition of various halogen derivatives to butadiene is not of the purely ionic type, but ionnomolecular in nature, in which polarization of the bonds during the process of addition does not attain complete dissociation in part of the added halogenated molecules. Depending upon the reaction conditions, the nature of the solvent, and that of the reagents, the ratio of the addition products formed ionically and molecularly may vary within wide limits. An important role in the addition process may apparently also be played by steric factors, whose importance was first pointed out by A.A. Petrov [4]. In the addition of halogen derivatives to homologs of butadiene and its derivatives with various substituent groups that are much more highly polarized than butadiene itself, addition occurs, apparently, only ionically, step-by-step; the addition reactions and the corresponding substitution reactions, in which we may suppose that the same intermediate carbonium ions are formed, result in the same ratios of isomeric halides, approaching their ratios in the equilibrium mixtures attained in the processes of thermal and catalytic isomerization.

EXPERIMENTAL

(with T. Galanina)

Addition of alpha chloroethyl methyl ether to butadiene. The following ingredients: 104 g of 1,3-butadiene (95%), 182 g of alpha chloroethyl methyl ether, and 2.9 g of freshly fused, pulverized zinc chloride, were successively added to a glass bottle immersed in a freezing mixture. The reaction mixture was allowed to stand in the freezing mixture for 10-15 hours. The ice melted during the first 5-6 hours, the reaction mixture remaining at room temperature for the remaining 5-10 hours. After this time had elapsed, the bottle containing the reaction mixture was again immersed in a freezing mixture, agitated vigorously a few times, and allowed to stand for 1-2 days. The end of the reaction was indicated by a drop of pressure inside the bottle. When the reaction was over, the reaction mixture was treated with several portions of water, its color changing from dark brown to light yellow. Then it was extracted with ether, the ether extract being dried over calcium chloride, the ether driven off, and the residue distilled in vacuo through a Widmer dephlegmator. Repeated fractionation yielded 30.4 g of 2-methoxy-4-chlorohexene-5 with a b.p. of 50° at 13 mm.

n_D^{20} 1.4349; d_4^{20} 0.9554; MR_D 40.54; calculated 40.45.
0.1934 g substance: 0.1832 g AgCl. Found %: Cl 23.5. $C_7H_{13}OCl$. Calculated %: Cl 23.9.

We also secured 41.8 g of 2-methoxy-6-chlorohexene-4 with a b.p. of 71° at 13 mm.

n_D^{20} 1.4539; d_4^{20} 0.9787; MR_D 41.11; calculated 40.45.
0.2042 g substance: 0.1939 g AgCl. Found %: Cl 23.6. $C_7H_{13}OCl$. Calculated %: Cl 23.9.

The residue consisted of a large quantity of high-boiling fractions plus tar.

Addition of alpha chloroethyl ethyl ether to butadiene. In this reaction we used 49 g of butadiene, 98 g of chloroethyl ethyl ether, and 1.5 g of pulverized zinc chloride. The procedure used in the reaction resembled that described for the preceding test. Repeated fractionations of the reaction products with a Widmer dephlegmator yielded 38.5 g of 2-ethoxy-4-chlorohexene-5 with a b.p. of 51-52° at 8 mm.

n_D^{20} 1.4334; d_4^{20} 0.9316; MR_D 45.38, calculated 45.07.
0.1990 g substance: 0.1718 g AgCl. Found %: Cl 21.4 $C_8H_{15}OCl$. Calculated %: Cl 21.8.

We also secured 41.2 g of 2-ethoxy-6-chlorohexene-4 with a b.p. of 71-72° at 10 mm.

n_D^{20} 1.4470; d_4^{20} 0.9535; MR_D 45.53; calculated 45.07.
0.1972 g substance: 0.1706 g AgCl. Found %: Cl 21.4. $C_8H_{15}OCl$. Calculated %: Cl 21.8.

The residue consisted of high-boiling fractions plus tar.

Addition of alpha chloroethyl n-butyl ether to butadiene. We used 42 g of butadiene, 104 g of alpha chloroethyl n-butyl ether, and 1.47 g of zinc chloride in this reaction. The reaction and the processing and fractionation of the reaction mixture, performed as in the preceding tests, yielded 24.9 g of 2-butoxy-4-chlorohexene-6 with a b.p. of 76-78° at 7 mm.

n_D^{20} 1.4382; d_4^{20} 0.9174; MR_D 54.52; calculated 54.31.
0.1990 g substance: 0.1480 g AgCl. Found %: Cl 18.4. $C_{10}H_{19}OCl$. Calculated %: Cl 18.6.

We also secured 34.2 g of 2-butoxy-6-chlorohexene-4 with a b.p. of 97-99° at 6 mm.

n_D^{20} 1.4510; d_4^{20} 0.9353; MR_D 54.84; calculated 54.31.
0.2049 g substance: 0.1507 g AgCl. Found %: Cl 18.2. $C_{10}H_{19}OCl$. Calculated %: Cl 18.6.

Action of KOH upon 2-methoxy-6-chlorohexene-4 dissolved in ethyl alcohol. 12 grams of KOH was dissolved in 160 g of ethyl alcohol, and 27 g of 2-methoxy-6-chlorohexene-4 was added to the resulting solution. An abundant precipitate of potassium chloride was thrown down within a few minutes, after which the reaction mixture was heated for two hours on a water bath. Then the alcohol was driven off, and the residue left in the flask treated with water and extracted with ether. After the ether layer had been dried and the ether driven off, the residue was fractionated in vacuo, yielding 18.2 g of 2-methoxy-6-ethoxyhexene-4 with a b.p. of 65-68° at 7 mm.

n_D^{20} 1.4304; d_4^{20} 0.8739; MR_D 46.77; calculated 46.35.
0.12 g substance: 0.3202 g CO_2; 0.1273 g H_2O. Found %: C 67.95; H 11.08. $C_9H_{18}O_2$.
Calculated %: C 68.25; H 11.39.

Action of KOH upon 2-methoxy-4-chlorohexene-5 dissolved in ethyl alcohol. 14 grams of KOH was dissolved in 160 g of ethyl alcohol, and then 30 g of 2-methoxy-4-chlorohexene-5 was gradually added. The reaction mixture was heated on a water bath for four hours. After the alcohol had been driven off, the residue was treated with water and extracted with ether. The alcoholic distillate was likewise treated with water and extracted with ether. The ether extracts were combined and dried over calcium chloride, after which the ether was driven off, and the residue fractionated in vacuo with a Widmer dephlegmator. This yielded 8.5 g of 2-methoxyhexadiene-3,5 with a b.p. of 60-61° at 93 mm.

n_D^{20} 1.4465; d_4^{20} 0.8132; MR_D 36.76; calculated 35.12; exaltation 1.6.
0.1258 g substance: 0.3446 g CO_2; 0.1162 g H_2O. Found %: C 74.76; H 10.35. $C_6H_{12}O$.
Calculated %: C 75.00; H 10.70.

We also recovered a mixture of ethers.

Action of maleic anhydride upon 2-methoxyhexadiene-3,5. 2.6 grams of 2-methoxyhexadiene-3,5 and 2.27 g of maleic anhydride were placed in a small round-bottomed flask. When the flask was gently heated over the flame of an alcohol lamp, a violent reaction set in, the temperature of the reaction mass rising to 170°. Fractionation of the reaction mixture yielded 2.7 g of an addition product with a b.p. of 168-170° at 8 mm.

n_D^{20} 1.4873.

0.1052 g substance: 0.2418 g CO_2; 0.0600 g H_2O. Found %: C 62.72; H 6.38. $C_{11}H_{14}O_4$. Calculated %: C 62.85; H 6.67.

TABLE 1

Time from start of isomerization, days	2-Methoxy-4-chlorohexene-5						2-Methoxy-6-chlorohexene-4	
	0.2% $ZnCl_2$ (0.0022 mole)		0.6% $ZnCl_2$ (0.0066 mole)		1.12% $ZnCl_2$ (0.012 mole)		1.12% $ZnCl_2$ (0.012 mole)	
	n_D^{20}	% of chloride isomerized	n_D^{20}	% of chloride isomerized	n_D^{20}	% of chloride isomerized	n_D^{20}	% of chloride isomerized
1	–	–	1.4393	25.2	1.4435	45.2	–	–
4	–	–	1.4421	37.8	1.4464	60.5	–	–
9	1.4363	10.0	1.4441	48.4	1.4475	66.3	1.4532	3.6
23	1.4378	15.2	1.4461	58.9	–	–	–	–
33	1.4388	20.5	1.4472	64.7	1.4486	72.1	1.4525	7.3
56	1.4411	32.6	1.4484	71.0	1.4500	79.4	–	–
77	1.4428	41.5	1.4492	75.2	1.4509	84.2	1.4525	7.3
120	1.4451	53.6	1.4506	82.6	1.4520	90.0	1.4525	7.3

TABLE 2

Time from start of isomerization, days	0.49% $ZnCl_2$		1.23% $ZnCl_2$	
	n_D^{20}	% of chloride isomerized	n_D^{20}	% of chloride isomerized
1	1.4364	7.9	1.4388	20.5
3	1.4371	11.5	1.4391	22.1
4	1.4373	12.6	1.4394	23.6
8	1.4375	13.6	1.4396	24.7
14	1.4380	16.3	1.4402	27.8

Catalytic isomerization of the methoxychlorohexenes. In our study of catalytic isomerization we used isomeric methoxychlorohexenes with the following constants: 2-methoxy-4-chlorohexene-5 with a b.p. of 50° at 13 mm; n_D^{20} 1.4349; d_4^{20} 0.9554 and 2-methoxy-6-chlorohexene-4 with a b.p. of 71° at 13 mm; n_D^{20} 1.4539; d_4^{20} 0.9787. Isomerization was effected in the presence of zinc chloride by the method described in our previous papers [6,7]. The percentage of isomeric chlorides in the reaction mixtures was calculated from the measurements of the refractive index. The first series of tests was run at +20°; the results are listed in Table 1.

The catalytic isomerization of 2-methoxy-4-chlorohexene-5 in the presence of zinc chloride at 0° is shown in Table 2.

SUMMARY

1. A study has been made of the addition of α-chloroethyl methyl, α-chloroethyl ethyl, and α-chloroethyl butyl ethers to butadiene, the corresponding 1,2 and 1,4 addition products being isolated and identified.

2. A study has been made of the catalytic isomerization of the isomeric methoxychlorohexenes in the presence of zinc chloride. 90-93% of 2-methoxy-6-chlorohexene-4 is in equilibrium with 7-10% of 2-methoxy-4-chlorohexene-5.

3. The order of addition of alpha chloroethyl methyl ether to butadiene has been determined. 65-75% of the haolgen ether is added at the 1,2 position, with 25-35% added at the 1,4 position.

4. The existing notions of the mechanisms involved in the addition of halogen derivatives to butadiene are subjected to a critical review. The opinion is expressed that the alpha halogen ethers and other halogen derivatives are added to butadiene ionnomolecularly rather than ionically.

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Laboratory of Organic Chemistry,
Kazan State University

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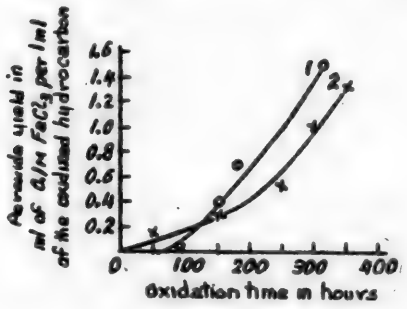
n-BUTYLBENZENE PEROXIDE

K. I. Ivanov, V. K. Savinova, and V. P. Zhakhovskaya

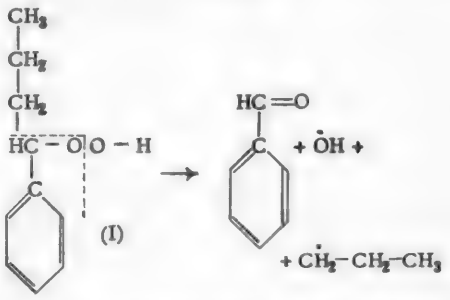
Of the peroxides of derivatives of the higher monoalkylbenzenes, only two tertiary hydroperoxides are known up to the present time, namely: isopropylbenzene hydroperoxide [1] and 2-phenylbutane hydroperoxide [2], which are produced fairly readily by oxidizing the respective hydrocarbons containing tertiary carbon atoms in the side chain at the alpha position with molecular oxygen.

In this connection we were interested in exploring the reaction with oxygen of benzene hydrocarbons containing an unbranched side chain, which do not possess readily peroxidized aliphatic tertiary C–H groups, and in studying the structure of the peroxides initially formed in this reaction. With this in mind we undertook the oxidation of n-butylbenzene by bubbling oxygen through it at 80° and irradiating it with ultraviolet light. Though this hydrocarbon begins to oxidize in the pure state under these conditions much later than secondary butylbenzene (it exhibits a long induction period), the accumulation of the peroxide takes place more rapidly later on (see figure). Adding some of the already oxidized hydrocarbon or some of its peroxide speeds up the oxidizing process considerably.

The peroxide formed as the initial product in the photooxidation of n-butylbenzene is a hydroperoxide with an OO–H group attached to the alpha carbon atom in the side chain (I).



Accumulation of peroxides in the oxidation of normal (I) and secondary (II) butylbenzenes in ultraviolet light at 80°.



The hydroperoxide of n-butylbenzene (1-phenylbutane hydroperoxide-1) is a colorless, transparent, rather viscous liquid that is readily soluble in organic solvents and nearly insoluble in water. The hydroperoxide of n-butylbenzene reacts even with a dilute aqueous solution of sodium hydroxide, yielding a sodium salt. When a hydrocarbon solution of the peroxide is treated with a concentrated (30%) solution of sodium hydroxide, the salt is precipitated as white crystals, which quickly deliquesce in air. When an aqueous solution of the salt is decomposed in the cold by dilute mineral acids, we recover the initial hydroperoxide.

When the hydroperoxide is boiled with a solution of ferrous sulfate, it is decomposed, yielding benzaldehyde, thus proving that the OOH group is at the alpha position. The hydroxyl and propyl radicals arising thereby (see the equation) can apparently condense partially, giving rise to n-propyl alcohol, and partially react in other ways.

The results of our investigation of the structure of the peroxide produced in the autocondensation of n-butylbenzene indicate that the molecular oxygen is first added to the α-carbon atom of the higher monoalkylbenzenes even when the latter is not a tertiary carbon atom but a much less reactive secondary one.

EXPERIMENTAL

Preparation of n-butylbenzene. 300 ml of anhydrous ethyl ether was added to 100 g of finely cut metallic sodium in a 1-liter Pyrex flask fitted with a reflux condenser, and then a mixture of 240 g of n-butyl bromide and 240 g of bromobenzene, both previously refined by fractionation and drying, was added. The reaction was violent at first, so that the flask had to be cooled. After 15-20 hours a straight condenser was substituted for the reflux one, and the ether was first driven out of the reaction mixture (on a water bath), after which a 170-185° fraction was collected. This fraction was then fractionated with a Hahn dephlegmator. The 181-184° fraction collected was redistilled at reduced pressure into a one-meter heated column, with an efficiency of 16 theoretical plates, and a packing consisting of cylinders 2 mm in diameter and 3 mm high, twisted from copper screening. The principal fraction, boiling at 70-70.5° at 10 mm, was pure n-butylbenzene with a d_4^{20} 0.8609 and n_D^{20} 1.4900 (b.p. 184° at atmospheric pressure).

Synthesis of n-butylbenzene peroxide. The normal butylbenzene was oxidized in two quartz flasks, fitted with reflux condensers and each containing 180 g of the hydrocarbon, by bubbling oxygen through at the rate of 5 ml per min. and at 80° while the flasks were irradiated by the ultraviolet light of a mercury lamp. After 440 hours of treatment the amount of active oxygen in the oxidized product was equivalent to 1.4-1.6% of the peroxide.

The peroxide concentrate (60 g) left after the bulk of the unreacted hydrocarbon had been driven off in vacuo (about 5/6 of the total volume) was an intense yellow. It was agitated twice with 8 ml and twice with 4 ml of a 0.25% aqueous solution of NaOH and twice with 4 ml of water to eliminate the coloring impurities. Then the decolorized product was treated five times in a separatory funnel with 0.25 its volume of a 7% aqueous solution of sodium hydroxide. The combined alkaline extracts were chilled to 0° and neutralized with 10% sulfuric acid, after which they were treated with ether (twice with 0.25 volume portions). The solvent was driven out of the ether extract after the latter had been dried over calcined sodium sulfate. The residue was fractionated at high vacuum from a small Claisen flask with a wide outlet tube sealed in at a low level. After the small overhead fraction had been distilled, the bulk of the product distilled at 56° (0.006 mm); it was the pure n-butylbenzene peroxide.

d_4^{20} 1.016; n_D^{20} 1.5103. MR_D 48.94; calculated 48.49 [1]
0.2764 g substance: 0.7246 g CO_2; 0.2108 g H_2O. 0.1276 g substance; 21.90 g benzene: Δt 0.178°.
Found %: C 71.70; H 8.54; M 166.9. $C_{10}H_{14}O_2$. Calculated %: C 72.26; H 8.48; M 166.2

The percentage of active oxygen (determined by the stannometric method) was equivalent to the consumption of 19.7 ml of 0.1N $FeCl_3$ per millimole. For $C_{10}H_{13}$—OO—H 20 ml of 0.1 N $FeCl_3$ has been calculated per millimole.

The hydroperoxide of n-butylbenzene exhibits qualitative reactions for active oxygen (evolution of iodine from a solution of potassium iodide, coloring a thiocyanate solution) and for a hydroperoxide group with zinc tetraacetate.

Decomposition of n-butylbenzene peroxide. 0.6 g of the hydroperoxide was boiled for 4 hours with 15 ml of a 25% aqueous solution of $FeSO_4 \cdot 7H_2O$ in a small flask fitted with a reflux condenser. After standing overnight, the product was fractionated with steam. A heavy yellow liquid (0.3 g), exhibiting the characteristic odor of bitter almonds and consisting of benzaldehyde, as proved by the following tests, accumulated in the distillate beneath an upper aqueous layer.

1. 6 ml of a solution of p-nitrophenylhydrazine (1 g of p-nitrophenylhydrazine in 50 ml of 50% acetic acid) was added to 0.1 g of the liquid. The abundant orange precipitate of the hydrazone that settled out at once was filtered out on a Schott filter, washed with water, twice recrystallized from alcohol, and dried at 80°; m.p. 189°. Its mixed melting point with the specially prepared p-nitrophenylhydrazone of benzaldehyde (m.p. 192°) was 190°.

2. 0.1 gram of the liquid was added to a solution of 0.3 g of dimedon in 15 ml of 50% ethyl alcohol. The white precipitate that settled out 6 hours later was twice recrystallized from dilute alcohol. M.p. 193°. The mixed melting point with the benzaldehyde (m.p. 192°) derivative prepared in the same way was 193°.

[1] By the method described previously [3].

SUMMARY

It has been shown that the photooxidation of n-butylbenzene by oxygen at 80° results in the formation of a hydroperoxide with an —OOH group attached to the alpha carbon atom in the side chain. The hydroperoxide of n-butylbenzene has been isolated and identified.

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The F. E. Dzerzhinsky All-Union Institute of Heat Engineering

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METHODS OF PRODUCING DIALKYL PEROXIDES

TETRALYL ETHYL PEROXIDE AND PHENYL ISOPROPYL ETHYL PEROXIDE

K. I. Ivanov and T. A. Blagova

Our inadequate knowledge of the dialkyl peroxides, especially the peroxides with mixed hydrocarbon radicals, is due to the imperfection of the methods hitherto employed in their preparation, so that the number of compounds of this type known up to the present time is extremely limited.

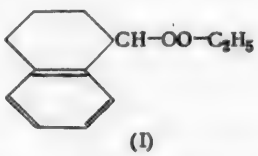
The method of alkylating hydrogen peroxides with dialkyl sulfates, as employed by Hock and Lang [1], for example, in synthesizing tetralyl methyl, cyclohexenyl methyl, p-menthenyl methyl, and hydrindenyl methyl peroxides, always involves the partial disintegration of the initial hydroperoxide by the reagent. This diminishes the yield of the synthesized peroxide and entails the difficult purification of the latter to eliminate the resultant decomposition products. Moreover, the distillation of the reaction product required during the course of the synthesis then involves the danger of the explosive decomposition of the peroxide produced, due to the presence of even traces of the unreacted dialkyl sulfate.

In our search for better methods of synthesizing dialkyl peroxides, we have made use of the action of alkyl halides upon alkaline salts of the hydrogen peroxides:

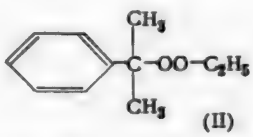
$$R{-}OO{-}Na + HalR_1 = R{-}OO{-}R_1 + NaHal.$$

This method proved to be free of the disadvantages enumerated above and to be quite convenient for the synthesis in particular, of the alkyl derivatives of alpha aryl-substitution derivatives of alkyl hydrogen peroxides, which readily form alkaline salts that in many cases can be isolated in the pure crystalline state without difficulty. We have worked out the conditions required for this synthesis; in particular, we have found that the reaction proceeds smoothly at room temperature in methanol, which satisfactorily dissolves both the initial sodium salts of the hydrogen peroxides and the alkyl halides. The latter must be used in excess to ensure a high yield of the synthesized peroxide. The NaHal produced in the reaction is precipitated under the given conditions. The resulting $R{-}OO{-}R_1$ peroxide is recovered by diluting the filtrate with water and is refined by distillation or other methods.

Starting with tetralin hydrogen peroxide and isopropylbenzene hydrogen peroxide, we produced tetralyl ethyl peroxide (I) and phenyl isopropyl ethyl peroxide (II), hitherto not described in the literature, as far back as 1948 [2]:



(I)



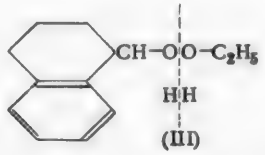
(II)

In the pure state, both of these compounds are colorless liquids with the acrid odor that is characteristic of organic peroxides, which do not solidify when chilled to -18°. They exhibit intensive qualitative reactions for peroxide oxygen, though they do not react with lead tetraacetate (proof that no hydrogen peroxide group is present). Both of the peroxides are fairly inert chemically, as is typical of H_2O_2 derivatives in which both of the hydrogen atoms have been replaced by hydrocarbon radicals. Only part of their active oxygen, namely, 19.2% in the tetralyl ethyl and 70% in the phenyl isopropyl ethyl peroxides, can be detected iodometrically

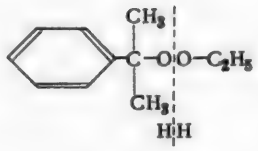
(even in the severe conditions we have worked out especially[1]). The stannometric method yields results that are still lower for the second of these compounds (22% for the tetralyl ethyl peroxide and 30% for the phenyl isopropyl ethyl peroxide).

Tetralyl ethyl peroxide (d_4^{20} 1.0696; n_D^{20} 1.5321) is distinguished from the phenyl isopropyl ethyl peroxide (b.p. 41.5° at 0.03 mm; d_4^{20} 0.9842; n_D^{20} 1.4960) by its higher viscosity. It also has a higher boiling point, though it is less stable at higher temperatures, so that it cannot be distilled without partial decomposition, even at high vacuum (0.005 mm).

Reduction of both peroxides with hydrogen in statu nascendi confirmed their structures by the production of the following: the first one yielded ethyl alcohol and alpha tetralol (Formula III), while the second yielded ethyl alcohol and dimethylphenylcarbinol (Formula IV).



(III)



(IV)

EXPERIMENTAL

Tetralyl Ethyl Peroxide. Synthesis. 5 ml of a 37% aqueous solution of NaOH was added at 0°, with vigorous stirring, to 12 g of pure (m.p. 56°) tetralin hydrogen peroxide (prepared by catalytically oxidizing tetralin by the method developed by one of the present authors together with V. Savinova and E. Mikhailova [3]), dissolved in 100 ml of benzene that contained no thiophene. The precipitated salt was filtered out at once and washed with benzene on a Buchner funnel. The resulting sodium salt of tetralin hydrogen peroxide was pressed out between sheets of filter paper (yield of about 8 g) and then dissolved in 150 ml of methanol that had been previously dried with calcined sodium sulfate and distilled. The solution, which was slightly cloudy, was allowed to stand in the dark at room temperature for 40 hours after 35 g (a 6.5-fold excess) of anhydrous ethyl bromide had been added to it. After the precipitated NaBr had been filtered out, the solution was diluted with 1.5 volumes of distilled water. The small lower layer that separated out, consisting of a solution of the peroxide in an excess of ethyl bromide, was separated from the upper water-alcohol layer, which was triply extracted with 0.5-volume portions of distilled diethyl ether. The lower layer was combined with the ether extracts of the upper layer, washed with distilled water, and thoroughly dried with calcined sulfate (the latter being frequently replaced by fresh batches). Then the ether and the ethyl bromide were driven out of the mixture at reduced pressure on a water bath. The residue (totaling some 5 g) was kept for two hours at 1 mm pressure and room temperature. The 14 grams of the crude product (n_D^{20} 1.5480) accumulated in this manner was freed of the tetralone and other impurities it contained by dissolving it in the minimum quantity of 88% methanol and triple extraction with 0.3-volume portions of petroleum ether with a b.p. below 63°. The combined petroleum ether extracts were washed with 0.3 volume of water and dried with calcined sulfate, after which the solvent was driven off in vacuo (at room temperature). Repurification by the procedure outlined yielded 6.5 g of a residue with n_D^{20} 1.5328. Final refining (dissolution in 100 ml of 76% aqueous acetone and a single extraction with 50 ml of petroleum ether) yielded 5.5 g of a product with n_D^{20} 1.5320. The product (which was faintly yellowish) was decolorized by dissolving it in 6 ml of methanol and agitating the solution for 20 minutes with 0.6 g of finely pulverized activated charcoal. The whole was filtered after one hour had passed, and the solvent was driven out of the filtrate by distillation in vacuo. The residue was a colorless, transparent, viscous liquid that did not solidify when chilled to -18°; it was tetralyl ethyl peroxide: d_4^{20} 1.0694; n_D^{20} 1.5321; δ (specific dispersion) $= \frac{n_F - n_C}{d} \cdot 10^4 = 145.9$.

0.2372 g substance: 0.6542 g CO_2; 0.1806 g H_2O. 0.2104 g substance; 20.772 g benzene: Δt 0.272°. Found %: C 75.22; H 8.52; O (by difference) 16.26; M 190.0. $C_{12}H_{16}O_2$. Calculated %: C 74.98; H 8.39; O 16.64; M 192.2.

Tetralyl ethyl peroxide exhibits a strong qualitative reaction for active oxygen (evolution of iodine from a neutral KI solution; coloring of a thiocyanate solution). Its reaction for a hydrogen peroxide group with

[1] Heating a sample of the peroxide with KI and hydrochloric acid in alcoholic solution for two hours to 50° in an atmosphere of CO_2 prior to titration with hyposulfite.

lead tetraacetate is negative. A drop of the peroxide burns in a Bunsen burner flame with a gentle smoky flame.

When tetralyl ethyl peroxide is heated above 80°, it decomposes, giving rise to liquid and gaseous products. It distills (with partial decomposition) at 55° at 0.005 mm (water bath warmed to 82°).

Tetralyl ethyl peroxide is soluble in ether, benzene, petroleum ether, methanol, ethyl alcohol, acetone, and CCl_4; it is insoluble in water.

Reduction. A small amount of distilled water was poured into 1.1 g of the peroxide distilled in 27 ml of concentrated acetic acid(until turbidity appeared, which disappeared upon heating). After 1 g of zinc dust was added, the mixture was refluxed for 30 minutes in a small flask fitted with ground-glass reflux condenser. Then the liquid in the flask, which did not exhibit a qualitative reaction for active hydrogen, was carefully decanted from the unreacted zinc and neutralized with 25% KOH.

The resultant precipitate was filtered out, and the lightest portion (3 ml) of the filtrate was driven off into a three-bulb Glinsky dephlegmator. The residue was treated twice with diethyl ether. The ether extract was washed with water and dried with calcined sulfate, and then the solvent was driven off. The remaining oily, yellowish liquid (0.6 g) was refluxed at 80-90° for 2 hours with 0.4 g of phenyl isocyanate. Then the mixture was steam-distilled to drive off the volatile components, the residue being extracted with petroleum ether. Evaporation of the solvent yielded white crystals, whose m.p. was 120.8° after double recrystallization from petroleum ether. The mixed melting point with the phenylurethane of specially synthesized alpha tetralol (m.p. 121.0°) was 120.8°.

The volatile reduction products were analyzed by treating a new portion of the peroxide (0.7 g) with hydrogen in status nascendi in the same vessel, but this time the upper end of the reflux condenser was connected to a trap (Petri bottle) containing 2 ml of distilled water, and the mixture with 0.7 g of zinc dust and 25 ml of 7% sulfuric acid (instead of acetic acid) was heated for 18 minutes. The reaction product, which was decanted from the zinc and then neutralized, was distilled (with a Glinsky three-bulb dephlegmator), the lightest portion (3 ml) being driven off. The water in the trap was added to the resultant aqueous distillate, the water-insoluble products were removed by extraction with petroleum ether, 0.5 g of p-nitrobenzoyl chloride and 3 ml of benzene were added, and the mixture was vigorously agitated with 0.9 ml of 20% aqueous NaOH. The upper (benzene) layer that collected upon standing was separated. When the benzene was allowed to evaporate from a watch glass, what was left was ethyl p-nitrobenzoate, which crystallized upon chilling; its m.p. was 55.5° after double recrystallization from petroleum ether. The mixed melting point with pure ethyl p-nitrobenzoate (m.p. 56°) was 55.7°.

Phenyl Isopropyl Ethyl Peroxide. Synthesis. 20.9 g of pure isopropylbenzene hydrogenperoxide, n_D^{20} 1.5244 (prepared by the thermal oxidation of isopropylbenzene [4]), was dissolved in 160 ml of benzene. The solution was placed in a three-necked flask fitted with a thermometer and a stirrer and chilled to +2° and then stirred vigorously while 23 g of similarly chilled 30% aqueous NaOH was gradually added (without allowing the temperature to rise above 8°). The precipitated sodium salt of isopropylbenzene hydrogenperoxide was filtered out in a Buchner funnel, washed with benzene, and dried between sheets of filter paper. The resultant salt (totaling about 36 g) was dissolved in 400 g of pure anhydrous methanol, and 40 g (more than 100% excess) of dried ethyl bromide was added. After the mixture had stood for 40-60 hours in the dark at room temperature, the precipitated crystals of NaBr were filtered out, and 15 volumes of water were added to the filtrate. The resultant lower layer was separated, and the upper layer was triple-extracted with 0.3-volume portions of diethyl ether. The ether extracts were washed with distilled water, combined with the lower layer, and then dried for 3 days with calcined sulfate (the sulfate being replaced twice by fresh batches). The barely yellowish, viscous liquid (14.2 g)[1] that remained after the ether and ethyl bromide had been driven off in a vacuum established by a water pump was fractionated at high vacuum from a Claisen flask made of molybdenum glass, fitted with

1) We have observed that in some instances the reaction is not complete, the product containing some isopropyl hydrogen peroxide (which arises, apparently, as the result of hydrolysis of the unreacted salt), as evidenced by its higher refractive index and its ability to react weakly with lead tetraacetate. The product can be freed of its hydrogen peroxide by treating its (1:4) benzene solution in the cold two or three times with a few ml of a 30% NaOH solution, and then processing it 5 or 6 times with half its volume of a 7% NaOH solution. Then it is washed with water and dried, the solvent is driven off, and the residue is fractionated at a high vacuum as described above.

a wide outlet tube (the water-bath temperature not exceeding 54°). After the first runnings had been distilled, the bulk of the product distilled at constant temperature. This principal fraction (11 g), which had a b.p. of 41.5° at 0.03 mm, was a colorless, transparent, mobile liquid that did not solidify when chilled to -18° and consisted of phenyl isopropyl ethyl peroxide: d_4^{20} 0.9842; n_D^{20} 1.4960; (specific dispersion) = $\delta = \frac{n_F - n_C}{d} \cdot 10^4 = 134.7$.

0.1962 g substance: 0.5276 g CO_2; 0.1586 g H_2O. 0.1248 g substance; 20.45 g benzene: Δt 0.174°. Found %: C 73.34; H 9.05; O (by difference) 17.61; M 178.9. $C_{11}H_{16}O_2$. Calculated %: C 73.30; H 8.95; O 17.75; M 180.2.

Phenyl isopropyl ethyl peroxide exhibits strong qualitative reactions for active oxygen (liberating iodine from a neutral KI solution and coloring a thiocyanate solution). Its reaction with lead tetraacetate is negative, evidence that no hydrogen peroxide group is present. When a drop of the peroxide is burned, it burns with a quiet, smoking flame.

Phenyl isopropyl ethyl peroxide is a fairly stable compound.

A sample of the pure peroxide suffered hardly any changes in its constants (specific gravity and refractive index) when kept for 19 months in a glass vessel at room temperature in our laboratory.

Phenyl isopropyl ethyl peroxide is soluble in ether, benzene, petroleum ether, methanol, ethyl alcohol, acetone, and CCl_4; it is insoluble in water.

Reduction. Two grams of the peroxide was dissolved in 54 ml of concentrated acetic acid. Distilled water was gradually added to the solution until a turbidity that vanishes upon heating appears. After 2.4 g of zinc dust had been added to the mixture, it was heated for 25 minutes in a flask fitted with a ground-glass reflux condenser. After a check for the absence of any reaction for active oxygen, the liquid was decanted from the unreacted zinc dust in the flask and neutralized with a 20% solution of NaOH. After the precipitate thrown down had been filtered out, the filtrate was treated twice with diethyl ether. The ether extract was washed with water and dried with calcined sulfate, after which the solvent was driven off on a water bath. The residue (0.6 g) was distilled in vacuo from a miniature Wurtz flask. The bulk of the distillate, which had a boiling point of 68° at 4 mm, crystallized. The melting point of the crystals was 26° after they had been pressed out between sheets of filter paper. The mixed melting point with dimethylphenylcarbinol (m.p. 26.5°) synthesized by the Klages method [5] was 26°.

The volatile products of reduction were analyzed by reducing a new portion of the peroxide (1.0 g) with zinc in the presence of sulfuric acid, as described above for tetralyl ethyl peroxide. The first (light) fraction secured in distilling the reduction product was treated with p-nitrobenzoyl chloride, yielding a p-nitrobenzoate, which had a m.p. of 56°. The mixed melting point with the ethyl ester of p-nitrobenzoic acid (m.p. 57°) was 57°.

SUMMARY

1. A method has been suggested and worked out to synthesize dialkyl peroxides by reacting alkaline salts of the hydrogen peroxides with alkyl halides dissolved in methanol.

2. Tetralyl ethyl and phenyl isopropyl ethyl peroxides, hitherto not described in the literature, have been synthesized and identified.

3. The structure of these peroxides has been established.

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The F.E. Dzerzhinsky All-Union Research Institute of Heat Engineering.

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THE POLYMERIZATION OF RING-SUBSTITUTED HALOGEN DERIVATIVES OF STYRENE

M. M. Koton, E. P. Moskvina and F. S. Florinsky

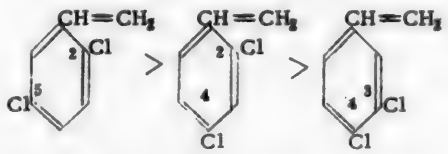
There are no systematic investigations of the physicochemical properties and the polymerizability of the dichlorostyrenes in the literature, despite the practical and theoretical interest attaching to such a study. The papers by Rutkovsky [1] and Marvel [2] contain very brief information in the properties of polydichlorostyrenes. We set as our goal the synthesis and the study of the polymerizability of three dichlorostyrenes: 2,5-dichlorostyrene, 2,4-dichlorostyrene, and 3,4-dichlorostyrene, as we had previously shown [3] that the isomers of halogen-substituted styrenes exhibit different polymerization rates. The constants of the dichlorostyrenes we synthesized are given in Table 1.

TABLE 1

No.	Name	Boiling point	Specific gravity at 20°
1	2,5-Dichlorostyrene	90-94° (5 mm) 72-73 (2 mm)	1.246
2	2,4-Dichlorostyrene	80-81 (6 mm)	1.249
3	3,4-Dichlorostyrene	92 (6 mm)	1.256

The samples tested contained 99.1-99.5% of the monomer. We studied the polymerization of the dichlorostyrenes at 75, 100, and 125° with no catalysts present, under the same conditions as those reported in our first report [3]. Our results indicate (see graphs) that introducing two chlorine atoms into the styrene's benzene ring increases the rate of polymerization substantially. When we compare the polymerization rates of dichlorostyrenes and monochlorostyrenes [3], we see that the introduction of a second chlorine atom into the styrene's benzene ring increases the polymerization rate by a factor of three, on the average. Moreover, the isomerism of the basic molecules of the halogen-substituted styrenes is of tremendous importance in this connection. In the monochlorostyrenes, the ortho isomer exhibits the higher polymerization rate, while in the dichlorostyrenes, the 2,5-dichlorostyrene exhibits the highest polymerization rate and the 3,4-dichlorostyrene the lowest rate. At 100°, for example, 3 hours of polymerization yields 72.3% of the polymer of 2,5-dichlorostyrene, 64.3% of the polymer of 2,4-dichlorostyrene, and 37.3% of the polymer of 3,4-dichlorostyrene while styrene itself yields 8% of the polymer.

The dichlorostyrenes may therefore be arranged in the following series in order of increasing rate of polymerization:



If we take the mean values, we find that 2,5-dichlorostyrene is polymerized 6 times as fast as pure styrene, while 2,4-dichlorostyrene is polyermized 5 times as fast and 3,4-dichlorostyrene is polymerized 3 times as fast. 2,5-Dichlorostyrene, in turn, is polymerized twice as fast as 3,4-dichlorostyrene. The differences between the rates of polymerization of the isomeric dichlorostyrenes, on the one hand, and the isomeric ortho and para monochlorostyrenes, on the other, are indisputable evidence of the presence of a special "ortho effect" (o-chlorostyrene, 2,5-dichlorostyrene, and 2,4-dichlorostyrene), manifested not only as polymerizability but also in some other instances.

The effect of temperature upon the rate of polymerization of the dichlorostyrenes is likewise of interest. At 75°, for example, 58% of 2,5-dichlorostyrene is converted into a polymer, within 10 hours, whereas the same result is achieved at 100° within 2 hours, and within less than 30 minutes at 125°.

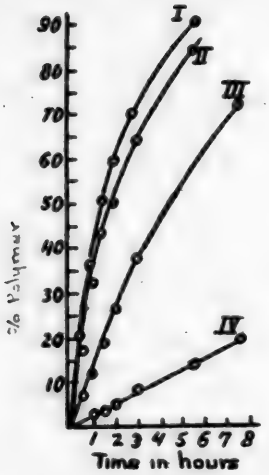


Fig. 1. Polymerization of dichlorostyrenes at 100°. I) 2,5-dichlorostyrenes; II) 2,4-dichlorostyrene; III) 3,4-dichlorostyrene; IV) styrene.

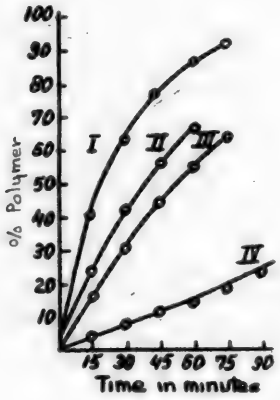


Fig. 2. Polymerization of dichlorostyrenes at 125°. I) 2,5-dichlorostyrene; II) 2,4-dichlorostyrene; III) 3,4-dichlorostyrene; IV) styrene.

TABLE 2

Molecular Weights of Polydichlorostyrenes

No.	Temperature	Time, hours	2,5-Dichlorostyrene		2,4-Dichlorostyrene		3,4-Dichlorostyrene	
			n_{sp}	Molecular weight	n_{sp}	Molecular weight	n_{sp}	Molecular weight
1	75°	5	1.1990	66611	0.4623	25683	–	–
2	75°	7	1.2070	67055	0.4929	27383	–	–
3	75°	10	1.5331	85172	0.5271	29283	–	–
4	100	1.5	1.1077	61538	0.4758	26433	–	–
5	100	3.5	1.1479	63772	0.5015	27861	0.5454	30300
6	100	5.5	1.1607	64483	0.5659	31438	0.5531	30727
7	100	7.5	1.3070	72611	0.6189	34383	0.5645	31361
8	125	0.25	0.9352	51955	–	–	–	–
9	125	0.50	1.0515	58416	0.3042	16900	–	–
10	125	0.75	0.9220	51222	–	–	0.4696	26088
11	125	1.00	0.9066	50366	0.4051	22505	–	–

Notes. 1. The molecular weights of the polydichlorostyrenes were determined after they had been precipitated with methanol from benzene solutions and dried to constant weight.

2. The molecular weights of the polymers of the 2,5- and 2,4-dichlorostyrenes were determined in benzene solutions, while that of the polymer of 3,4-dichlorostyrene was determined in a chloroform solution.

3. The equation $n_{sp} = K_m CM$, where $K_m = 1.80 \cdot 10^{-4}$, was used in our calculations.

Measurements of the molecular weights of the polydichlorostyrenes (Table 2) indicate that the polymers of 2,5-dichlorostyrene have the highest molecular weight, of the order of 60,000 to 85,000, while the molecular weights of the polymers of the 2,4- and 3,4-dichlorostyrenes range from 26,000 to 31,000.

The polymers of the dichlorostyrenes are transparent and colorless and have a rather high softening point (160-180° in a capillary). The polymers of the 2,5- and 2,4-dichlorostyrenes are soluble in benzene, toluene, xylene, carbon tetrachloride and chloroform, while the polymer of 3,4-dichlorostyrene is soluble only in chloroform.

Study of the kinetics of polymerization of the dichlorostyrenes indicates that this process is a first-order reaction.

We calculated the activation energies for the isomeric dichlorostyrenes, as shown in Table 3.

TABLE 3

No.	Name	Activation energy Cal/mole
1	2,5-Dichlorostyrene	16.97
2	2,4-Dichlorostyrene	15.55
3	3,4-Dichlorostyrene	15.56
4	Styrene	20.13

These figures indicate that the introduction of two chlorine atoms into the styrene benzene ring diminishes the activation energy of the polymerization process.

SUMMARY

1. A study has been made of the polymerization of the 2,5-, 2,4-, and 3,4-dichlorostyrenes at 75, 100, and 125° with no catalysts present.

2. The introduction of two chlorine atoms into styrene's benzene ring greatly increases the polymerization rate of the substitution derivatives of styrene.

3. The highest polymerization rate is exhibited by 2,5-dichlorostyrene, with 3,4-dichlorostyrene having the lowest rate.

4. The introduction of chlorine atoms into styrene's benzene ring diminishes the activation energy of the polymerization process.

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The Leningrad Institute of Technical Physics
of the U.S.S.R. Academy of Sciences

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SYNTHESIS OF TRIARYL PHOSPHINES AND TRIARYL PHOSPHINOXIDES USING ORGANOLITHIUM COMPOUNDS

B. M. Mikhailov and N. F. Kucherova

The only carbocyclic phosphorus compounds known at the present time with the phosphorous atom attached to the aromatic ring are derivatives of benzene and naphthalene, no more complex compounds in which the condensed systems contain more than two benzene rings being known.

Setting as our objective the production of organophosphorous compounds of polycyclic hydrocarbons, we undertook a systematic testing of methods of synthesizing phosphorous derivatives; the example of anthracene convinced us of their unsuitability for use with polycyclic systems. We found, for instance, that anthracene does not react with phosporous trichloride in the presence of aluminum chloride; anthracene reacts with phosphorus pentachloride to constitute chlorine derivatives rather than phosphorus compounds [1], as might have been expected by analogy with unsaturated hydrocarbons; in this case, the method of synthesizing alkyl and aryl methylphosphinic acids developed by A.E. Arbuzov [2] is obviously unusable because of the low mobility of a halogen atom in halogen derivatives of aromatic hydrocarbons; and lastly, phosphorus derivatives of anthracene can not be produced by reacting an organomagnesium reagent with phosphorus trichloride [3]. We set about determining the feasibility of using lithium reagents in the synthesis of phosphorus compounds and found that they are highly effective agents for the synthesis of various classes of carbocyclic organophosphorus compounds.

The present paper describes a method of synthesizing triaryl phosphines and oxides of triaryl phosphines by means of lithium reagents, that makes it possible to synthesize compounds of this type in the tricyclic and tetracyclic series of hydrocarbons, hitherto unknown, in addition to those in the monocyclic and bicyclic series, which can be obtained by other methods of synthesis as well.

The method employed in synthesizing these groups of phosphorus compounds involves the action of organolithium compounds of aromatic hydrocarbons upon phosphorus trichloride (to produce triaryl phosphines) and upon phosphorus oxychloride (to produce triaryl phosphine oxides). The method was first tried out on the simplest types of these compounds — phenyllithium and α-naphthyllithium — after which it was applied to more complicated compounds.

Aryl lithium compounds react with phosphorus trichloride to produce triaryl phosphines as follows:

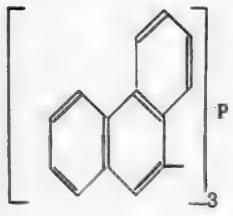
$$3ArLi + PCl_3 = Ar_3P + 3LiCl.$$

The reaction is carried out by adding an ether solution of phosphorus trichloride to an ether solution or a suspension in ether of the organolithium compound, prepared from the aryl halide and metallic lithium (for phenyllithium and α-naphthyllithium) or n-butyllithium (for the other aryl lithium compounds). In some instances the reagents were mixed together in the inverse order. When we react 3 equivalents of phenyllithium with phosphorous trichloride, we can secure 61% of the theoretical yield of triphenylphosphine. Pfeiffer [4] used an organomagnesium compound when he secured a poor yield (about 12%) of triphenylphosphine, an appreciable yield of triphenylphosphine being obtained only when an excess of phenylmagnesium bromide was employed [5].

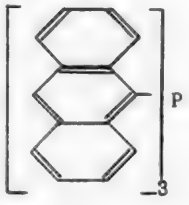
The reaction is not as smooth when α-naphthyllithium is employed, the yield of tri-(α-naphthyl)-phosphine being only 27%. This compound has been described by Anschutz and his co-workers, who synthesized it from α-naphthylmagnesium bromide and phosphorus trichloride.

Reacting 9-phenanthryllithium with phosphorus trichloride yields tri-(9-phenanthryl)-phosphine (I), the yield being 72% of the theoretical.

We have synthesized the following derivatives of anthracene: tri-(9-anthryl)-phosphine (II) and tri-(9-bromoanthryl-10)-phosphine (III) The yield of the former from 9-anthryllithium totaled 20%; together with the phosphine we secured about the same quantity of anthracene, which is evidence of the complexity of the reaction between phosphorus trichloride and 9-anthryllithium. We synthesized the compound (III) by reacting 9-bromoanthryl-10-lithium, prepared by reacting 9,10-dibromoanthracene and phenyllithium together with PCl_3.



(I)



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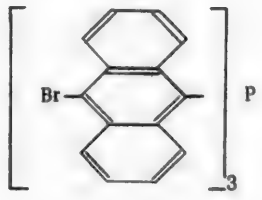

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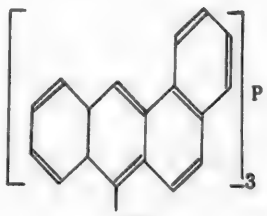


(IV)

Tri-(1,2-benzanthryl)-phosphine (IV) was synthesized similarly, the yield being 55% of the theoretical.

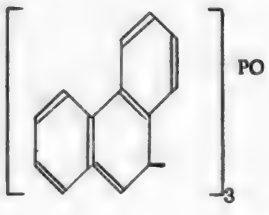
The reaction of aryl lithium compounds with phosphorous oxychloride in ether results in the formation of triaryl phosphine oxides, as follows:

$$3ArLi + POCl_3 = Ar_3PO + 3LiCl.$$

Triphenylphosphine oxide was synthesized by this method, with a yield of 65%, i.e., the same yield as when a Grignard reagent was used [6].

Tri-(α-naphthyl)-phosphine oxide, synthesized by the use of organomagnesium compounds [7] (no yield being stated), is produced by reacting α-naphthyllithium with phosphorus oxychloride, the yield being 38% of the theoretical.

A derivative of a tricyclic hydrocarbon—tri-(9-phenanthryl)-phosphine oxide—and a derivative of a tetracyclic hydrocarbon—tri-(1,2-benzanthryl)-phosphine (VI)—have been secured with satisfactory yields by this same method.



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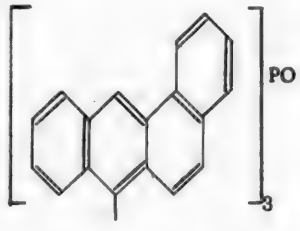

(VI)

EXPERIMENTAL

All operations with organolithium compounds were performed in a nitrogen atmosphere. A two-necked ampoule was used as the reaction vessel in all cases.

Triphenylphosphine. A solution of phenyllithium, prepared from 5 g of bromobenzene, 0.44 g of lithium, and 30 ml of absolute ether was stirred and chilled with snow and salt while 1.3 g of phosphorus trichloride diluted with 20 ml of absolute ether was added during the course of 15-20 minutes. Considerable heat was evolved, the ether solution turning yellow. The reaction mass was decomposed with water, the ether extract being separated and washed with a 10% NaOH solution and then with water, and the ether driven off. The residue, 4.6 g of an oil, crystallized when alcohol was added to it. The substance was filtered out (1.9 g; m. p. 72-74°) and crystallized from alcohol. This yielded 1.7 g of triphenylphosphine as colorless lamellae with a m.p. of 77-78°. The yield was 61.3%, based on the bromobenzene used in the reaction.

Tri (α-naphthyl)-phosphine. A solution of α-naphthyllithium, prepared from 4 g of α-bromonaphthalene, 0.27 g of lithium, and 55 ml of absolute ether, was chilled with snow and salt and vigorously stirred while an ether solution (50 ml) of 0.8 g of phosphorus trichloride was added during the course of half an hour. No heat was evolved, and the reaction mass gradually turned a greenish-yellow. When the reaction was finished, the mixture was stirred while water was added, after which a dilute solution of alkali was added until the reaction was alkaline, and the ether extract was separated, washed with water, and dried with anhydrous sodium sulfate. The ether was driven off until the volume totaled 7-10 ml, and the precipitate was filtered out. This yielded 0.7 g (26.9%) of tri-(α-naphthyl)-phosphine with an m.p. of 276-278°. The product is slightly soluble in ordinary organic solvents and crystallizes from a large quantity of chloroform as a molecular compound with the formula of $(C_{10}H_7)_3P \cdot CHCl_3$ and an m.p. of 260-262°. After the tri-(α-naphthyl)-phosphine had been heated to 110° for several hours, it lost its solvent and had an m.p. of 276-278°, which agrees with the figure given in the literature.

Tri-(9-phenanthryl)-phosphine. 5 grams of 9-bromophenanthrene (m.p. 63-64°) was added in a current of nitrogen to a freshly prepared and filtered solution of butyllithium (made from 3 g of n-butyl chloride, 0.5 g of lithium, and 30 ml of absolute ether). The 9-phenanthryllithium settled out as a white crystalline precipitate that was insoluble in ether. The phenanthryllithium was allowed to settle for a few minutes, and then the ether layer was decanted and the organolithium compound twice extracted with ether (30 ml) and decanted. The washed 9-phenanthryllithium was suspended in 40 ml of ether, and 0.9 g of phosphorus trichloride diluted with 20 ml of absolute ether was added, with constant agitation, during the course of 15-20 minutes. Considerable heat was evolved, and the reaction mass first turned pink and then red. After half the phosphorus trichloride had been added, a precipitate began to settle out, and the color slowly disappeared. The reaction mass was decomposed with water, and the resultant precipitate was filtered out. This yielded 3.32 g of a substance with an m.p. of 358-365°. Double recrystallization from toluene yielded 2.6 g of tri-(9-phenanthryl)-phosphine as colorless lamellae with an m.p. of 374-376°. The yield was 72% of the theoretical, based on the 9-bromophenanthrene used for the reaction.

0.1177 g substance: 0.3638 g $(NH_4)_3PO_4 \cdot 12\,MoO_3$. Found %: P 5.12. $C_{42}H_{27}P$. Calculated %: P 5.53.

Tri-(9-anthryl)-phosphine. 5 grams of 9-bromoanthracene (m.p. 98-100°) was added to a freshly prepared and filtered solution of butyllithium (made from 3 g of n-butyl chloride, 0.5 g of lithium, and 30 ml of absolute ether). 0.9 g of phosphorus trichloride, diluted with 25 ml of absolute ether, was gradually added, with agitation and chilling with ice, to the resultant 9-anthryllithium, which had settled out as a yellow precipitate. During the course of the reaction the color of the reaction mass changed from green to brown-red. The reaction mass was decomposed with water, the ether solution washed with a little water, and half of the ether driven off. The precipitated orange-red crystalline deposit was filtered out (1.25 g; m.p. 160-240°), while the mother liquor was evaporated to a total volume of 10-12 ml. This precipitated 0.5 g of a substance with an m.p. of 160-205°. The product with an m.p. of 160-240° was twice recrystallized from benzene, yielding 0.84 g of tri-(9-anthryl)-phosphine as orange-red lamellae with an m.p. of 270-273° (20% yield).

0.0464 g substance: 0.1553 g $(NH_4)_3PO_4 \cdot 12MoO_3$. Found %: P 5.71. $C_{42}H_{27}P$. Calculated %: P 5.51.

The benzene mother liquors yielded 0.25 g of anthracene (m.p. 214-216°).

Crystallizing the fraction with a m.p. of 160-205° from benzene yielded another 0.4 g of anthracene (m.p. 213-215°). The anthracene totaled 18% of the theoretically possible.

Tri-(9-bromoanthryl-10)-phosphine. 5 g (0.014 mole) of 9,10-dibromoanthracene (m.p. 220-222°) was added to 32 ml of an ether solution of phenyllithium (0.017 mole). Twenty minutes later, an ether solution (15 ml) of 0.67 g of phosphorus trichloride was added to the ice-chilled and stirred solution. The addition of the first few drops turned the reaction mass red. A red precipitate was thrown down, its total increasing as the chloride was added. Ten minutes after the reagents had been mixed, the reaction mass was decomposed with water, and the crystalline precipitate (3.1 g; m.p. 160-200°) was filtered out. The latter was boiled with 250 ml of toluene, the solution then being filtered and cooled. As the solution stood, 1.2 g of tri-(9-bromoanthryl-10)-phosphine as lustrous orange-yellow lamellae with a m.p. of 205-208° settled out.

0.1645 g substance: 0.3524 g $(NH_4)_3PO_4 \cdot 12MoO_3$. Found %: P 3.48. $C_{42}H_{24}Br_3P$. Calculated %: P 3.88.

Tri-(1,2-benzanthryl)-phosphine. 2 g of 10-bromo-1,2-benzanthracene was added to a solution of n-butyllithium, prepared from 1.1 g of n-butyl chloride, 0.2 g of finely cut lithium, and 20 ml of absolute ether. An ether solution of 0.35 g of phosphorus trichloride was chilled and then gradually added to the resultant 1,2-benzanthryl-10-lithium [8]. The reaction, which involved the liberation of heat, was accompanied by the solution's

turning orange-yellow and by the precipitation, toward the end of the reaction, of an abundant light-yellow, amorphous precipitate. After the reaction mass had been treated with water, the finely crystalline precipitate (0.52 g) was filtered out, and the ether solution was concentrated to small volume. This yielded another 0.3 g of the substance as minute lamellae with a m.p. of 190-193°.

The synthesized substance was very sparingly soluble in organic solvents. The substance was treated with boiling benzene before being analyzed. M.p. 192-194°. The yield totaled 53%.

0.0822 g substance: 0.2247 g $(NH_4)_3PO_4 \cdot 12MoO_3$. Found %: P 4.49. $C_{54}H_{33}P$. Calculated %: P 4.35.

Triphenylphosphine oxide. A solution of phenyllithium (made from 5 g of bromobenzene, 0.44 g of lithium, and 30 ml of ether) was chilled with ice, and 1.6 g of phosphorus oxychloride, diluted with 20 ml of absolute ether, was added. The reaction is extremely violent, the solution turning a brown-black. Ten minutes later the reaction mass was poured into water. The amorphous precipitate that settled out at first gradually decomposed, and the reaction product was converted into an ether solution. The latter was treated with water, the ether was driven off until its volume was 1/4 of the original volume, and the precipitated substance was filtered out. This yielded 1.6 g of a substance with a m.p. of 152-154°. Another 0.45 g of a substance with a m.p. of 151-153° was recovered from the concentrated mother liquor. Crystallization from ether of both fractions yielded 1.7 g of triphenylphosphine with a m.p. of 155-157°. The yield totaled 65%, based on bromobenzene.

Tri-(α-naphthyl)-phosphine oxide. An ether solution of α-naphthyllithium, prepared from 8 g of α-bromonaphthalene, 0.54 g of lithium, and 45 ml of absolute ether, was chilled with ice and agitated while 1.6 g of phosphorus oxychloride in 20 ml of absolute ether was added. During the reaction the color changed from brown to coffee color, and an abundant precipitate settled out. The reaction mass was allowed to stand for half an hour at room temperature and then decomposed with water. The crystalline precipitate was filtered out (1.9 g, m.p. 305-312°), and the ether solution was washed with water and concentrated to 1/4 of its original volume. This yielded another 0.7 g of a substance with a m.p. of 296-305°. Double recrystallization from a large quantity of chloroform yielded 2.1 g (38.5%) of tri-(α-naphthyl)-phosphine, with a m.p. of 335-336.5°.

4.560 mg substance: 13.967 mg CO_2; 2.095 mg H_2O. Found %: C 83.59; H 5.14. $C_{30}H_{21}OP$. Calculated %: C 84.07; H 4.91.

Tri-(9-phenanthryl)-phosphine. 30 ml of absolute ether was added to freshly prepared 9-phenanthryllithium, prepared from 5 g of bromophenanthrene by the procedure described above and washed with ether, after which it was chilled and stirred while 0.9 g of phosphorus oxychloride diluted with 30 ml of ether was added. Considerable heat was liberated, and an amorphous white precipitate was thrown down. The reaction mass was set aside for 10 minutes and then decomposed with water. The colorless crystalline precipitate that formed at the boundary between the two layers was filtered out (3.1 g; m.p. 295-315°). Double recrystallization of the precipitate from toluene yielded 1.8 g of a colorless finely crystalline substance with a m.p. of 354-356°. The yield of the tri-(9-phenanthryl)-phosphine oxide was 49%, based on the 9-bromophenanthrene used for the reaction.

0.1934 g substance: 0.5960 g $(NH_4)_3PO_4 \cdot 12MoO_3$. Found %: P 5.27. $C_{42}H_{27}PO$. Calc.%: P.536.

Tri-(1,2-benzanthryl)-phosphine oxide. 0.5 g of phosphorus oxychloride, diluted with 40 ml of ether, was slowly added, with chilling, to 1,2-benzanthryl-10-lithium, prepared from 3 g of 10-bromo-1,2-benzanthracene and n-butyllithium [8]. As the reagent was added, the organolithium compound disappeared and an amorphous light-yellow precipitate settled out. After the reaction mass had been treated with water, the yellow precipitate floating between the ether and aqueous layers was filtered out and dried. This yielded 1.5 g of tri-(1,2-benzanthryl)-phosphine oxide, with a m.p. of 184-187°, or 63% of the theoretical. The substance was refined by crystallizing it from a benzene-ether mixture. It consisted of extremely minute light-yellow lamellae with a m.p. of 191-193°.

0.1188 g substance: 0.3102 g $(NH_4)_3PO_4 \cdot 12MoO_3$. Found %: P 4.36. $C_{54}H_{33}PO$. Calculated %: P 4.26.

SUMMARY

Organolithium reagents can be used in synthesizing carbocyclic compounds of phosphorus. Triaryl phosphines are synthesized by reacting phosphorus trichloride with aryl lithium compounds, while triaryl phosphine oxides are produced by reacting phosphorus oxychloride with aryl lithium compounds. This method makes it possible to synthesize the simplest compounds of this type, as well as phosphinic derivatives of tricyclic and tetracyclic hydrocarbons.

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Institute of Normal and Pathological Morphology,
USSR Academy of Medicine

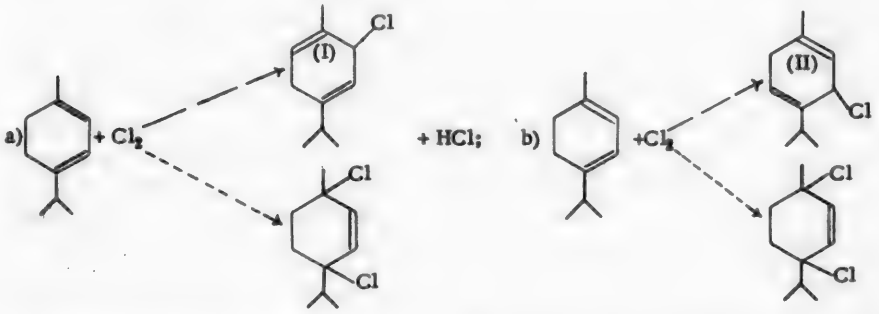
NEW TYPES OF TERPENE TRANSFORMATIONS

VI. THE ACTION OF CHLORINE UPON α-TERPINENE

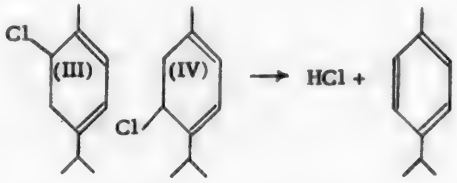
D. Tishchenko and N. Summ

In previous reports [1] we have described the action of chlorine upon α- and β-pinenes, dipentene, terpinolene, and Δ^3-carene. In all these cases, the principal reaction products proved to be unsaturated monochlorides with a shifted double bond, in conformity with the theoretical consideration we have developed. These initial terpenes have no conjugated double bonds; α-terpinene has such double bonds, but branched at the ends. In the light of the generally accepted notions of the interaction of conjugated dienes with halogens, we might have supposed that the action of chlorine upon α-terpinene would result in the addition of chlorine at the 1,4 position, yielding 1,4-dichloroparamenthene-2. There is no reason to think that addition will occur, in contrast to the Thiele rule, at the 1,2 and 3,4 positions, since the α-terpinene molecule has no sharply polar substituents. At the start of this research we had reason to believe, however, that the reaction can follow another course, as will be set forth later, viz.: the same "anomalous" M.D.Lvov reaction as exists for the terpenes mentioned above.

Both the double bonds of α-terpinene are equally branched, in contrast to the bonds in dipentene and terpinolene, so that two possibilities must be considered when we discuss the possible mechanism of the reaction:



Will these monochlorides be stable? We already know [1] that the monochlorides of terpinolene and carene are decomposed by heating above 50-60°, giving off hydrogen chloride. Morever, we know that the terpene monochlorides undergo an allyl rearrangement, if the latter is not prevented by the Bredt and semicyclic exclusion principles. There is no obstacle to such a rearrangement in the given case, so that we ought to obtain the chlorides (III) and (IV), respectively:



The two monochlorides (III) and (IV) are derivatives of dihydrobenzene and ought to be more readily decomposed, with the evolution of hydrogen chloride, than the monochlorides of terpinolene and carene, since this reaction results in the formation of p-cymene, an aromatic hydrocarbon, corresponding to a transition from dihydrobenzene to benzene. The latter transformation is accompanied by the liberation of energy, totaling some 20 cal per mole [2] ("ring aromatization energy").

If the supposed formation of p-cymene is borne out by experiment, it will constitute a new exception to the Thiele rule. Up to now the sole exception to this rule has been 1,2 addition. Our instance is an exception of no little theoretical significance. Its discovery compels us to re-examine the so-called resonance theory, even if this be supererogatory.

Even external observation of the reaction of chlorine with α-terpinene shows that this reaction differs from that involving the other terpenes mentioned above. The temperature of the reaction medium is kept within the −5 to −8° range, except for α-terpinene, when ice and snow are used for chilling, when the chlorine pass-through rate is the same, and when equal volumes of terpenes are treated in the same apparatus. In the case of α-terpinene the temperature rises rapidly to +15 and +25°; hence, the chlorine must be fed in at a much lower rate of flow in order to avoid overheating and to keep the temperature within the same boundaries of −5 to −8°. With all the terpenes the volumetric rate at which carbon dioxide is evolved is lower than the chlorine rate of supply, though it is higher in the case of α-terpinene. The percentage of the "anomalous" reaction did not exceed 90% for all the terpenes, while it fluctuated about 125% in the case of α-terpinene. This paradoxical figure is explained below.

After a few preliminary tests, we ran a pilot-plant experiment, using all precautions to ensure obtaining a true picture of the reaction (see the experimental section). Analysis of the reaction products fully confirmed the considerations set forth above. No monochloride was found; instead of it we found p-cymene, its yield being proportional to the "anomalous" reaction ($\frac{126}{2} = 63\%$). The residue consisted almost entirely of the dichloride. The dichloride yield approximated the calculated value (~37%). It should be noted that no hydrogen chloride was evolved during fractionation of the reaction products, as in the fractionation of the products of the chlorination of carene and terpinolene at high temperatures. Hence, at temperatures below −10°, the monochlorides (I) or (II) [(III) or (IV)] are decomposed at the instant they are produced in the reaction medium, two molecules of hydrogen chloride being evolved per molecule of p-cymene, thus explaining the high yield of the "anomalous" reaction (127%) which is absurd at first glance. As a matter of fact, the yield is half the figure given above.

The structure of the dichloride was established by ozonation followed by oxidation. Ozonating the dichloride with an excess of ozone and decomposing the ozonide with cold water in the presence of platinum black yielded a substance with the composition of $C_{10}H_{16}O_2Cl_2$, which exhibited aldehyde reactions. Oxidation of this substance with an alkaline solution of hydrogen peroxide oxidized the aldehydic groups to carboxyl ones, and saponified the two chlorine atoms, producing the dicarboxylic acid $C_{10}H_{18}O_6$. This information and the method of its synthesis indicate that the only structure it can be assigned is 2,5-dihydroxy-2-methyl-5-isopropyladipic acid, the initial dichloride being assigned the structure of 1,4-dichloroparamethene-2. Hence, the dichloride was formed by the addition of chlorine to α-terpinene at the 1,4 position, the entire course of the interaction of chlorine with α-terpinene being represented by the schema set forth above. This dichloride is a wholly stable substance that suffers no change in storage or when distilled in vacuo, so that there is no reason to believe that p-cymene is formed from the dichloride in our instance by splitting out two molecules of hydrogen chloride at temperatures below −10°.

Thus, our experimental data have fully confirmed the schema proposed by us for the action of chlorine upon α-terpinene and have discovered a new exception to the Thiele rule.

In conclusion, let us dwell upon the problem of the production of pure α-terpinene. When we turn to the pertinent literature [3], we find that different authors cite highly divergent constants for this terpene: b.p. from 170 to 181°; the d_4^{20} from 0.837 to 0.845 and even 0.855 (!) [4]. At the same time it may be noted that the same figures indicate that the samples of α-terpinene with a specific gravity below 0.842 produce a satisfactory yield of the characteristic nitrosite of α-terpinene, while their oxidation yields αδ-dihydroxy-α-methyl-δ-isopropyladipic acid; they also exhibit a rather appreciable exaltation of the molar refraction, as is typical of a substance with conjugated double bonds. These samples of α-terpinene were produced by detaching two molecules of hydrogen chloride from α-terpinene dihydrochloride by the action of alkalies or tertiary amines. The samples of α-terpinene produced by detaching two molecules of hydrogen chloride from α-terpinene dihydrochloride by the action of alkalies or tertiary amines. The samples of α-terpinene produced by dehydrating terpineol have a high specific gravity and do not produce high yields of the nitrosite or the above-named acid.

It was natural to suppose that dehydration of terpineol would yield, in addition to α-terpineol and terpinolene, 1,8-cineole, with a sp.gr. of 0.930 and a b.p. of 174.5°, which does not react with sodium. To check these inaccuracies we prepared 1.5 kg of the terpineol dehydration product and fractionated it at 11 mm pressure into a column with an efficiency of about 20 theoretical trays and a reflux ratio of 12-15. The fractions with a b.p. of 55-58° furnished a good yield of the nitrosite and an oily, decomposable polybromide (characteristic of α-terpinene); the high-boiling fractions yielded no nitrosite, but did yield a crystalline tetrabromide that is characteristic of terpinolene. The α-terpinene fractions boiled at from 172.5° to 174.5° at atmospheric pressure and had a sp.gr. of 0.848 to 0.845, i.e., was clearly unusable. Analysis showed that these fractions contained 3.5 to 4% of oxygen, i.e., about 30% of cineole. We know that cineole constitutes a molecular compound with

resorcinol [5] with the composition of $(C_{10}H_{16}O_2)_2 \cdot C_6H_6O_2$ and a m.p. of 80-85°, and, hence, stable below that temperature. Treating these fractions twice with an excess of resorcinol and driving off the α-terpinene in vacuo from the cineole complex, followed by rectification into a column, yielded a sample of α-terpinene with the following constants: b.p. 31.5° at 1 mm and 172.5-173.5° at 760 mm; d_4^{20} 0.8398; n_D^{20} 1.4770; MR_D 45.80; calculated 45.24; ΣMR_D 0.56. The constants cited for the purest α-terpinene (as given by the MR_D and the specific gravity) are [6]: b.p. 173.5-174.8°; d_4^{20} 0.8375; n_D^{20} 1.477; MR_D 45.88; ΣMR_D 0.64.

EXPERIMENTAL

The α-terpinene was chlorinated in the manner described [1]. 310 g of α-terpinene, 192 g of $NaHCO_3$, and 70.5 g of chlorine were used. As a result of chilling with snow and salt and of reducing the chlorine rate of flow, the temperature within the reaction mixture did not exceed −10°. The reaction product totaled 325 g, including 25.85 g of chlorine and 45.68 g of chlorine in the form of salts; percentage of anomalous reaction = 126.7.

The excess terpinene was driven off at 0.5 mm with a small packing and a bath temperature that did not exceed 35° (the collector being chilled with snow and salt), the residue totaling 74 g. It was first fractionated molecularly (bath temperature not over 40°). The distillate totaled 57 g, the residue 12 g, and the losses 5 g. The distillate was fractionated into a herringbone column with 2 cm clearance (to avoid loss of vacuum in the flask due to dynamic resistances in the column) at a pressure of $1 \cdot 10^{-6}$ mm. This yielded 12.5 g of a fraction up to 27° (principally 24-27°), 32 g of a 27-31° fraction, plus a residue of 2.5 g and a loss of 10.0 g (bath temperature not above 40°).

For the 27-31° fraction: d_4^{20} 1.007; n_D^{20} 1.4966. Found %: Cl 33.4. $C_{10}H_{16}Cl_2$. Calculated %: Cl 34.6.

Analysis of the hydrocarbon fraction distilled from the chlorination product (242 g). The terpenes were eliminated from 100 ml (85 g) by triple agitation with an equal volume of sulfuric acid (sp.gr. 1.73), which dissolves the terpenes but does not act upon the aromatic hydrocarbons. The first agitation evolved considerable heat, less being evolved in the second agitation, and none in the third. The oily layer was driven off with steam, and the hydrocarbon dried and distilled. It all boiled at 175-176° (33 g); its constants were: d_4^{20} 0.855; d_4^{13} 0.8606; n_D^{13} 1.4922. Oxidizing the hydrocarbon yielded p-hydroxypropylbenzoic acid, with the constants that are typical of that acid; hence, the hydrocarbon was p-cymene. It totaled 86.8 g. If we take the high-boiling residue to be a dichloride, which is quite close to actuality, its yield was 74 g. The possible yields were: monochloride $136 \cdot 0.69 \cdot \frac{170}{136}$ = 107 g, of which $136 \cdot 0.63 \cdot \frac{134}{136}$ = 84.4 g of cymene; $136 \cdot 0.37 \cdot \frac{207}{136}$ = 76.6 g of the dichloride, where 136 is the weight of the terpinene reacting with 1 g of chlorine; 0.63 = 63% = $\frac{126}{2}$ = the theoretical yield of the monochloride; 0.37 = the theoretical yield of the dichloride; 136, 170, 207, and 134 are the respective molecular weights of terpinene, the monochloride, the dichloride, and cymene.

Investigation of the structure of the dichloride. Ozonation. 5 g of the dichloride in chloroform was chilled with snow and salt and saturated with ozone (44 liters, containing 5% of ozone). The chloroform was driven off in vacuum, and the ozonide decomposed with ice water containing platinum black until its reaction for a peroxide was negative. The water-insoluble substance weighed 6.0 g and exhibited aldehyde reactions.

Found %: Cl 26.6, 26.1; C 48.0, 47.8; H 7.1, 7.0. $C_{10}H_{16}O_2Cl_2$. Calc.%: Cl 29.7; C 50.2; H 6.7.

2.7 g was stirred with an excess of an alkaline solution of hydrogen peroxide until it dissolved. The solution was acidulated and extracted with ether, and the ether was driven off. The residue crystallized and contained no chlorine.

Found %: C 51.4, 51.5; H 7.8, 7.8. $C_{10}H_{18}O_6$. Calculated %: C 51.3; H 7.7.

The acid was decomposed by treating it with lead peroxide, carbon dioxide being liberated; hence, it was an α-hydroxy acid. The silver salt of the acid was prepared in the usual manner.

Found %: Ag 47.9. $C_{10}H_{16}O_6Ag_2$. Calculated %: Ag 48.2

Synthesis of α-terpinene. 1800 g of terpineol was added a drop at a time to a boiling saturated solution of oxalic acid. The distillate contained 1556 g of oil. The latter was distilled from a Würtz flask at 2 mm, the 37-48° fraction totaling 1462 g.

This fraction was fractionated at 11 mm into a column with an efficiency of 20 theoretical trays and a reflux ratio of 8. After three fractionations we secured (see table):

Fraction No.	B.p.	Wt. (g)	B.p. at 760 mm	d_4^{20}	Production of nitrosite	Bromination
I	51–56°	39	Up to 173°	0.851	–	Liquid, decomposes
II	56	203	172.5–174	0.848	M.p. 154°	"
III	56–57.5	152	173.5–174.5	0.846		
IV	57.5–60	82	174–176	0.845	Little	
V	60–65	–	–	–	None	Crystals
VI	65–68	–	–	–	None	

Fractions II, III, and IV were combined and heated on a water bath with 20% of their aggregate weight of resorcinol, with stirring. Within two hours the resorcinol deliquesced into a heavy oil, after which the *a*-terpinene was driven off at 1 mm from the coordination compound, and the above procedure was repeated (not all the resorcinol deliquesced). The *a*-terpinene driven off was fractionated at 1 mm in the column mentioned above, a fraction with a b.p. of 31.5° being collected (325 g). The high-boiling fractions yielded pure terpinolene, as reported earlier [1]

SUMMARY

1. The action of chlorine upon *a*-terpinene has been investigated for the first time.

2. It has been shown that, in conformity with the theoretical considerations we have advanced, the principal reaction product is p-cymene, produced by the by-product 1,4-dichloro-p-menthene-2 splitting hydrogen chloride out of the chloride (I) or (II) after the latter had undergone an allyl rearrangement to the chloride (III) or (IV).

3. This demonstrates that the Thiele rule does not apply to this case, which constitutes a new type of the rule's inapplicability.

4. A method is set forth for securing pure *a*-terpinene from terpineol.

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[3] Cf. Auwers. Ber., 42, 2425 (1909) for summary; Simonsen. The Terpenes, Vol. I, p. 141-147.

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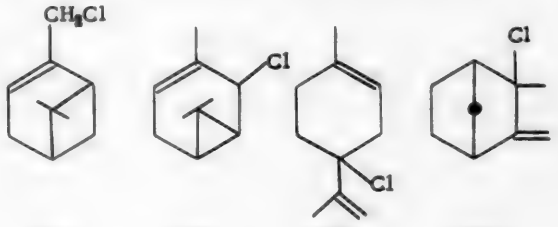
The S. M. Kirov Academy of Forest Technology

NEW TYPES OF TERPENE TRANSFORMATIONS

VII. THE SYNTHESIS OF ALCOHOLS AND ETHERS FROM CHLOROTERPENES

D. Tishchenko, A. Khovanskaya, and T. Danilova

In our preceding reports [1] we have described the synthesis of chloroterpenes, produced by reacting the terpenes with chlorine. These chlorides are terpene derivatives with the same degree of saturation and the same carbon skeleton as the original terpene, but with a shifted double bond, chlorides of the allylic type. In these papers we also have indicated the temperature range within which these chlorides are stable, set forth the possibility or impossibility of their allyl rearrangement (Bredt and semicyclic exclusion principles), and demonstrated that these latter conclusions are borne out by experiment. In our first report we noted that these allylic chloroterpenes may serve as the initial substances for the synthesis of various terpene derivatives possessing the same carbon skeleton and the same degree of unsaturation as the original terpene, their common formula being $C_{10}H_{15}X$, where X is any atom or group of atoms. Derivatives of this kind are either wholly unknown or else accessible only with difficulty at the present time. The present report sets forth some general considerations governing the anion exchange reactions of allylic chlorides and reports the results of our research on the synthesis of the respective alcohols and ethers, with the general formula of $C_{10}H_{15}X$, from 7-chloro-α-pinene (I), 3-chloro-Δ^4-carene (II), 4-chlorodipentene (III), and chloroisosantene (IV).



(I) (II) (III) (IV)

We have previously set forth considerations, which have been confirmed experimentally, to the effect that these chlorides must not undergo an allyl rearrangement when heated. These same considerations enable us to assert that no allyl rearrangement will occur when a chlorine atom is exchanged for any radical [the semicyclic exclusion principle in the chlorides (I) and (III); the elimination of the double bond conjugated to the three-membered ring in the chloride (II); and the greater strain existent in the structure of santene than in isosantene in the chloride (IV)]. As we shall see below, this prediction is borne out by experiment.

The conversion of allylic chlorides to any other derivatives in anion exchange reactions requires that we know the order of these reactions if we are to control them consciously. In 1939 one of the authors of the present paper found that the saponification of allyl chloride is a unimolecular reaction. The same was found to be the case with as-dichloromethylethylene [2]. This may serve as a basis for our supposing that the anion exchange reactions of all allylic chlorides, including our chloroterpenes, are unimolecular. The velocity that governs the rate of overall transformation will be the rate of dissociation of the allylic chloride into the chlorine anion and the organic cation. Then the latter will coordinate with another anion or with the anions present in the reaction medium; therefore, if our aim is a maximum yield of a given compound, we must see to it that the reaction medium contains no anions but the one whose derivative is the given compound. For example, as we shall demonstrate below, chloroterpenes must not be reacted with potassium acetate in an alcoholic solution, as we would get an appreciable percentage of an ether, in addition to the desired ester, notwithstanding the negligible concentration of the alkoxyl ion in the solution. Moreover these facts indirectly confirm the unimolecularity of the anion exchange reaction of our chloroterpenes.

The following relationship was established long ago for the velocities of the anion exchange reactions of saturated chlorides: tertiary $\gg$ secondary $>$ primary. The same holds true for the chloroterpenes, which are chlorides of an allylic type. In exchange reactions with potassium acetate the chloride (I) (primary) requires heating for four hours in an acetic acid solution (117°) if the reaction is to be complete; the chloride (II) requires only

two hours of heating, and the chlorides (III) and (IV) require only 20 minutes of heating at 50°, which is equivalent to approximately 10 seconds at 117°.

The direct saponification of the chloroterpenes (especially the primary and secondary ones) is not a convenient method of synthesizing the respective alcohols from them. The reaction drags out for dozens of hours, apparently because of the negligible solubility of the chloroterpenes in boiling water or in solutions of alkali carbonates, resulting in considerable tarring of the reaction products, and still the reaction remains incomplete. Inasmuch as the boiling points of the chloroterpenes lie in approximately the same range as those of the respective alcohols, they cannot be separated thoroughly by fractionation. We also get high-boiling products, evidently diterpenyl ethers. We therefore abandoned direct saponification and tried roundabout saponification, via the esters. This method yielded fully satisfactory results.

Putting this method into practice is not difficult: the chloroterpene is heated for some time to some temperature or other with a solution of anhydrous potassium acetate in anhydrous acetic acid. The precipitated potassium chloride, which is slightly soluble in the reaction medium, enables one to check the progress of the reaction: if the potassium chloride is suction-filtered out and the filtrate reheated, the absence of any newly formed precipitate indicates that the reaction is complete.

In the case of the chloride (I), the reaction follows a single path, producing only the acetate of myrtenol (7-hydroxy-α-pinene) boiling in an interval of one or two degrees. This chloride remains stable even at relatively high temperatures. The chlorides (II) and (III), which decomposed when heated yield $C_{10}H_{14}$ hydrocarbons as the result of the splitting out of hydrogen chloride, in addition to the corresponding esters. Though the chloride (IV) is stable when heated, it behaves in the same way, the yield of the hydrocarbon being smaller. We produced these hydrocarbons, "dehydroterpenes," from the same and from other chloroterpenes, as well as by different methods. They have the same composition as cymene, but are not aromatic hydrocarbons. Their properties are quite unusual.

In every case we secured acetates of the alcohols that are not products of an anion exchange involving an allyl rearrangement that occurs at the instant of exchange, the chloride (I) yielding an ester of pyrtenol, the chloride (II) an ester of 3-hydroxy-Δ^4-carene, the chloride (III) an ester of 4-hydroxydipentene, and the chloride (IV) an ester of tertiary isosantenol; in other words, the chlorine in these chlorides is replaced by an acetic acid residue with any rearrangement taking place, in agreement with the theoretical considerations referred to above.

The esters (I) and (III) ($OCOCH_3$ instead of Cl) smell like cedar oil (Juniperus virginiana); the ester (II) has the persistent and strong odor of eau de cologne, and the ester (IV) smells like camphor. The reaction product yields are below those expected, owing to their volatility with the solvent, acetic acid. If so desired, they may be extracted from the latter with light gasoline, after dilution with water. It is simpler and more satisfactory to repeat the operation on the driven-off acetic acid. The acetates are saponified by heating them with an alcoholic solution of an alkali. The yields of alcohols, based on the esters, are nearly quantitative.

It should be noted that the alcohols produced are apparently of very high purity. It has been said, for example, that the phenylurethane of myrtenol (isolated from the essential oil of myrtle) cannot be secured in crystalline form [3], though we have secured it in crystals; 114-115° is given as the melting point of myrtenyl acid phthalate [3], whereas the ester of our synthetic myrtenol has a m.p. of 117-118°. The phenylurethane of carenol (II) also crystallized within 24 hours after its synthesis. Anyone who has worked with terpene derivatives knows how hard it is to secure them in the crystalline state whenever they are not pure enough.

Myrtenol [(I), with OH replacing Cl] is known, but the alcohols (II), (III), and (IV) have been synthesized for the first time, which is true of their esters as well. Their synthesis, like that of carveol (see Report III), opens the way to various syntheses in the terpene and homoterpene series, based on the chloroterpenes synthesized for the first time.

It should be possible to synthesize ethers of terpene alcohols by reacting a sodium alcoholate dissolved in the respective alcohol upon the chloroterpenes. We have found that these ethers are secured with a fairly high yield by reacting chloroterpenes with an alcoholic solution of an alkali. This method was checked for the chloride (I): we secured the methyl, ethyl, and isoamyl ethers, hitherto unknown liquids with peculiar, unpleasant odors.

EXPERIMENTAL

Synthesis of myrtenol. (by D. Tishchenko). The chloride (I) had a b.p. of 85.5-87° at 11 mm; d_4^{20} 1.0065; n_D^{20} 1.4976; $[\alpha]_D^H$ (10 cm) = + 21.8°; its total chlorine was 19.9%, its active chlorine was 19.8%. Direct saponification: 50 g of the chloride, 15 g of chalk, 200 ml of water. The mixture was stirred in a flask fitted with a reflux

condenser on a boiling water bath until no more carbon dioxide was evolved (26 hours). The undissolved chalk totaled 4.2 g, the reaction being 74% complete. The 47 g of oil was separated and fractionated. It distilled below 120°, the first runnings containing chlorine, the middle fractions containing 8-9% of hydroxyl ($C_{10}H_{16}O$ contains 11.2% OH), the end fractions containing no hydroxyl. This method was discarded in view of its obvious unsuitability.

Synthesis of myrtenyl acetate. 1. Action of potassium acetate in methanol. 100 g of the chloride, 65 g of the fused salt (60 g called for theoretically), 300 ml of methanol. 36.6 g of KCl was precipitated after 8 hours of refluxing, with another 2.2 g settling out after another 8 hours. The solution was diluted with fourfold its volume of water and then extracted with ether. The aqueous solution was found to contain 2.3 g of KCl, making a total of 41.1 g; the possible total was 42.0 g. The ether was driven out of the ether layer, and the residue fractionated at 10 mm into a column with an efficiency of 4-5 theoretical trays. This yielded: Fraction I 81-83° — 29.0 g; Fraction II 83-110° — 12.6 g; Fraction III 110-112° — 51.2 g; and a residue of 5.2 g. Fraction I contained traces of chlorine.

Fraction I: d_4^{18} 0.937; n_D^{18} 1.4832.

Found %: C 78.7, 78.9; H 10.8, 10.8; OCH_3 16.5, 16.2. $C_{10}H_{15}OCH_3$. Calculated %: C 79.5; H 10.8; OCH_3 18.8.

Fraction III: d_4^{20} 0.989; n_D^{20} 1.4743; $[\alpha]_D^{16}$ (10 cm) = + 29.3°.

Found %: C 74.0, 74.1; H 9.4, 9.5; saponification value 282, 284. $C_{12}H_{18}O_2$.
Calculated %: C 74.2; H 9.3; saponification value 288.

The yield of the ether (Fraction II divided in half) was 37% of the theoretical, that of the ester being 51%.

2. The same in ethyl alcohol. See above for the quantities of reagents used and the experimental conditions. The methanol was replaced by ethyl alcohol. The reaction was 92% complete after 12 hours of boiling. We secured about 25% of the theoretical yield of ethyl myrtenyl ether [d_4^{20} 0.925; n_D^{20} 1.4728; $[\alpha]_D^{16}$ (10 cm) = + 10.7°; % OC_2H_5 21.8 and 21.6], and about 60% of myrtenyl acetate (d_4^{20} 0.990; n_D^{20} 1.4834; saponification value 286 and 287).

3. The same in acetic acid. 100 g of the chloride (I), 65 g of the fused salt, and 300 ml of acetic acid. The reaction was completed after 3.5 hours of refluxing. 39.8 g of KCl was found in the precipitate and the solution. The acetic acid was driven off in a water-jet vacuum with a herringbone packing, the residue being distilled with steam, and the oil being separated and fractionated at 20 mm into a column with an efficiency of 4-5 theoretical trays.

This yielded: 6.5 g of a fraction up to 120°; 82.3 g of a 120-122° fraction, and 5.0 g of residue. The fraction was myrtenyl acetate, as indicated by its constants (d_4^{20} 0.9905; n_D^{20} 1.4744, saponification value 286 and 286) and by its yielding myrtenol upon saponification (vide infra). The acetate yield was not below 72%. The principal losses were in the acetic acid driven off; when this acid was diluted with water, it grew turbid, an oily layer with the odor of myrtenyl acetate floating on top.

Saponification of myrtenyl acetate. 223 g of the acetate was refluxed in a flask on a boiling bath together with 75 g of potassium hydroxide and 400 ml of alcohol. The alcohol was driven off into a herringbone column, the residue diluted with water to make 1 liter and then extracted with ether, the ether being driven off and the residue fractionated at 13 mm into a column with an efficiency of 4-5 theoretical trays. This yielded: 5.0 g of a fraction up to 106.5°; 163.5 g of a 106.5-107° fraction; and 4.0 g of residue. The alcohol yield was at least 94%.

106.5-107° fraction: d_4^{20} 0.9746; n_D^{20} 1.4960; $[\alpha]_D^{15}$ (10 cm) = + 29.1°.

Found: MR_D 45.55. $C_{10}H_{15}OH\overline{\square}$. Calculated 45.43. Found %: C 78.6, 78.5; H 10.6, 10.4. $C_{10}H_{16}O$. Calculated %: C 78.8; H 10.5.

Myrtenyl acid phthalate. 5 g of phthalic anhydride was heated with 5 g of alcohol to 100° until they dissolved in each other. After the melt had solidified, it was treated with an aqueous soda solution, dissolving completely. The solution was acidulated, and the acid suction-filtered out, dried, and dissolved in chloroform. The undissolved residue totaled 0.15 g. The chloroform was driven off, and the crystals were recrystallized from boiling gasoline (80-100°). The m.p. was 113-115° after the first crystallization, being raised to 117-118° after the second and third crystallizations. The gram equivalent was found to be 300; the figure for $C_{18}H_{24}O_4$ is 300.

Inasmuch as secondary alcohols react with phthalic anhydride at temperatures above 125°, while tertiary alcohols do not [5], the alcohol must be taken to be a primary one.

Phenylurethane of myrtenol. 1 g of the alcohol was sealed into a tube with 1 g of phenyl isocyanate and heated to 100° for 1 hour. As the melt cooled, it hardened into a hyaline mass. The mass was dissolved in 50 ml of

gasoline (100-110°), and the solution was poured into a beaker. Practically all the contents crystallized within a month, after nearly all the gasoline had evaporated. The crystals were pressed out on paper and recrystallized from gasoline (30-50°) to a constant m.p. of 66-67° (clusters of thin prisms). Subsequent preparations crystallized as soon as a seed crystal was added.

Found %: N 5.3, 5.4. $C_{17}H_{21}O_2N$. Calculated %: N 5.1.

The structure of myrtenol was established by oxidizing it to myrtenal with chromic anhydride in acetic acid, the yield being satisfactory; the myrtenal yielded an oxime with the m.p. of 71-72° that is typical of myrtenaloxime [4]. The oxime was heated with acetic anhydride to convert it into myertenonitrile, which was saponified to myrtenic acid with a m.p. of 52-53° [4] and a gram equivalent of 169 (170 is the calculated value).

Synthesis of carenol (3-hydroxy-Δ^4-carene) (by A.Khovanskaya). Preliminary tests indicated that heating to 117° for 1.5 hours and 2.5-3 hours on a boiling bath would suffice to complete the reaction of the chloride (II) with potassium acetate. The yield of the acetate is low, totaling about 30%; a large percentage of low-boiling fractions of low specific gravity (about 0.9) and high refractive index (about 1.51) plus a viscous, nondistillable residue ("dehydroterpene" and its polymer) being obtained.

We used 20 g of the chloride (II) (%Cl = 17.6), 14 g of fused potassium acetate, and 100 ml of acetic acid. 2.5 hours of heating on a boiling bath. The reaction was more than 92% complete (6.7 g of KCl precipitated, the KCl in the solution being disregarded). The subsequent procedure was the same as that employed for myrtenol. The acetic acid driven off again grew turbid when diluted with water. After the low-boiling fractions (the "dehydroterpene") had been driven off, the acetate fraction was collected: b.p. 91-93° at 4 mm (6.3 g); d_4^{20} 0.987; n_D^{20} 1.4820; MR_D 56.06. $C_{10}H_{15}OCOCH_3$. Calculated: 55.10; ΣMR_D 0.96, indicating the presence of double bonds conjugated with the three-membered ring and the absence of an allyl rearrangement at the instant of the exchange reaction. The experimental saponification value was 282, the calculated value 288. Carenyl acetate is an oily liquid with a very pleasant flowery fragrance.

Saponification of carenyl acetate. 5.1 g of the ester was saponified by boiling it for 4 hours with an excess of alcoholic alkali, after which the alcohol was driven off on a water bath and the residue diluted with three times its weight of water and extracted with gasoline (30-50°). The gasoline was eliminated from the extract, and the residue was fractionated at 5 mm. The principal fraction (4.1 g) boiled at 91°; d_4^{20} 0.969; n_D^{20} 1.5001; MR_D 46.12 $C_{10}H_{15}OH$. Calculated 45.74. The alcohol yield was nearly quantitative. When the experiment was repeated, an alcohol with the following constants: m.p. 80-81° at 0.7 mm; d_4^{20} 0.967; n_D^{20} 1.4987; MR_D 46.12. The alcohol has a strong flowery odor and does not react with phthalic anhydride in boiling benzene; hence, it is not a primary alcohol [5].

Phenylurethane of carenol. 0.85 g of the alcohol was sealed into a test tube together with 0.7 g of phenyl isocyanate and heated on a boiling bath for 6 hours. The contents of the test tube crystallized completely within 24 hours. The contents dissolved completely in gasoline at 100° (no diphenylurea; the alcohol is not a tertiary one). As it cooled, crystals settled out. The m.p. was constant at 121° after a second crystallization.

Synthesis of the alcohols from the monochlorides of terpinolene (III) and santene (IV) (by T.Danilova).

Synthesis of dipentenol-4 via its acetic ester. Preliminary tests indicated that the reaction of the chloride (III) with potassium acetate is complete within 20 minutes at 50° or within 24 hours at 15°. Much less of the acetic ester is secured than of the "dehydroterpene" or its polymer.

We used 49 g of the chloride, 50 g of the potassium acetate, and 300 ml of acetic acid. The mixture was allowed to stand at 15° for 24 hours. The 15.3 g of KCl was suction-filtered out, the dissolved KCl being disregarded; the reaction was at least 87% complete. The solution was diluted with water to make 1 liter and then extracted with gasoline (30-50°), the gasoline being driven off and the residue fractionated into a column with an efficiency of 4-5 theoretical trays. This yielded 19.5 g of "dehydroterpene" fractions (d_4^{20} 0.90, n_D^{20} ~1.51), 6.5 g of a fraction with a b.p. of 40-41° at 0.1 mm (d_4^{20} 0.9740; n_D^{20} 1.4923), and 15.0 g of a nondistillable tacky residue (the "dehydroterpene" polymer). The dehydroterpene and its polymer totaled 34.5 g, and the yield of the acetate was 11%.

Saponifying the acetate. 11.2 g of the acetate (40-41° fraction at 0.1 mm in two runs) was heated to boiling for 4 hours with an excess of alcoholic alkali. The alcohol was driven off, and the residue diluted with water; then it was extracted with ether, the ether driven off, and the residue fractionated at 1 mm. This yielded 1.8 g up to 64°, 1.6 g at 64-69°, and 1.3 g at 69-73°.

Fraction constants: d_4^{20} 0.961, 0.967, 0.968; n_D^{20} 1.495, 1.503, 1.508; MR_D 46.22, 46.46, 46.99; % OH 8.3, 9.2, 9.4. $C_{10}H_{15}OH$. F_2. Calculated MR_D 46.77; % OH 11.2. Analysis of Fraction III (69-73°). Found %: C 77.9, 77.9; H 10.8, 10.6. $C_{10}H_{16}O$. Calculated %: C 78.9; H 10.6.

Fraction III did not react with phthalic anhydride in boiling benzene, heating it with phenyl isocyanate yielded diphenylurea, and it was not oxidized by chromic anhydride in acetic acid. Hence, it was a tertiary alcohol, with a structure corresponding to that of chloride (III)(dipentenol-4).

Synthesis of isosantenol. We began by determining that the chloride (IV) reacts nearly completely with potassium acetate in 20 minutes at 50° or in 24 hours at 15°.

We used 23 g of the chloride, 20 g of potassium acetate, and 150 g of acetic acid. The solution was heated to 50° and set aside to stand for 24 hours. The KCl suction-filtered out totaled 9.4 g, the reaction being no less than 86% complete. The filtrate was diluted with water to make half a liter and then extracted with gasoline (30-50°); the gasoline was driven off, leaving a residue of 22 g, which was fractionated into a small column. This yielded: 3.7 g of heads that polymerized in storage ("dehydroterpene", b.p. 30-64° at 7 mm); 14.5 g of fractions representing the acetate (d_4^{20} 1.0; b.p. 60-68° at 2 mm); and 2.6 g of residue. Refraction yielded the principal acetate fraction, with a b.p. of 72-74° at 4 mm; d_4^{20} 1.018; n_D^{20} 1.4773; MR_D 50.03; $C_9H_{13}OCOCH_3$. Calculated 49.78; ΣMR_D + 0.25; the experimental saponification value was 312, the calculated value being 312. The refraction exaltation indicated that a semicyclic double bond was present, as in the chloride (IV) (no allyl rearrangement occurring).

Saponifying isosantenyl acetate. 2 g of the ester was saponified by boiling it for 6 hours with an alcoholic alkali. This yielded an alcohol with a b.p. of 80-86° at 10 mm.

d_4^{20} 1.006; n_D^{20} 1.4972.

Found %: OH 11.5. $C_9H_{13}OH$. Calculated %: OH 12.5

The alcohol did not react with phthalic anhydride in boiling benzene, and smelled like camphor.

Synthesis of ethers of the $C_{10}H_{15}OR$ series. (by D. Tishchenko). The chloride (I) was used in developing this method, which involved heating the chloride with a 20% excess of alkali, dissolved in alcohol, until no more potassium chloride was precipitated. Heating had to be done for 5 hours with methanol, $2\frac{1}{2}$ hours with ethyl alcohol, and 1 hour with amyl alcohol. The recovery of the ether from the reaction mixture involved driving the alcohol off into a column, diluting the residue with water and extracting it with diethyl ether, driving the diethyl ether off, and fractionating in vacuo into a column. The yields of all three ethers were no less than 80%: they were mobile liquids with singular odors and had the following constants:

$C_{10}H_{15}OCH_3$: b.p. 79-81° at 7 mm; d_4^{20} 0.0936; n_D^{20} 1.4836. Found %: OCH_3 17.6, 17.2.

Calculated %: OCH_3 18.8. $C_{10}H_{15}OC_2H_5$: b.p. 94-95° at 15 mm. Found %: OC_2H_5 23.4, 23.0.
Calculated %: OC_2H_5 25.0.

$C_{10}H_{15}OC_5H_{11}$: b.p. 128-130° at 10 mm; d_4^{18} 0.895. Found %: C 81.2, 81.3; H 11.9, 11.7.
Calculated %: C 81.1; H 11.7.

SUMMARY

1. Some points are set forth concerning the anion exchange reactions of the allylic chloroterpenes we have synthesized.

2. It has been shown that saponifying the chloroterpenes with boiling water containing neutralizers is not a suitable method of producing the corresponding alcohols.

3. Reacting potassium acetate with the chloroterpenes in a solution of acetic acid yields acetates of the respective terpenes. The chloroterpenes that are unstable when heated (II and III, and to a lesser degree, IV) also yield "dehydroterpenes", C_nH_{2n-6}, hydrocarbons that are not aromatics.

4. Myrtenol, Δ^4-carenol-3, dipentenol-4, and tertiary isosantenol have been synthesized by saponifying the acetates. The latter three terpenols have been synthesized for the first time.

5. A method is given for synthesizing ethers of $C_{10}H_{15}OR$ terpenols.

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The S.M.Kirov Academy of Forest Technology

THE SYNTHESIS OF CYCLOHEPTANE-1,1-DICARBOXYLIC ACID VIA MALONIC ESTER

V. P. Golmov

In using the malonic synthesis to synthesize compounds whose molecules contain a four-membered ring, Golmov and Kazansky [1], Kazansky and Lukina [2], and Golmov [3] have shown that this reaction consists of two successive stages: the formation of a γ-halogen alkyl malonic ester by the action of sodium malonic ester upon a 1,3-dihalogen derivative, followed by its cyclization by a sodium alcoholate.

The rather low yield of a cyclic product secured when Kizhner's method [4] is employed is not due to the difficulty of constituting a four-membered ring, as is generally assumed, but to the side reactions that occur during the first stage of the synthesis; the yield of the four-membered ring is some 75% of the theoretical. The overall yield can be increased substantially by choosing conditions that insure a high yield of the intermediate product.

We were also interested in making a similar study of the reaction of sodium malonic ester with other halogen derivatives. This was particularly true of the 1,6-dihalogen derivatives, since we know from the literature [5] that the action of sodium malonic ester upon hexamethylene bromide yields a minute percentage of cyclopentane-1,1-dicarboxylic ester (which has not been isolated in the pure state).

Our previous study of this problem made it seem likely that we could raise the yield of this cyclic product, too, by splitting this reaction into two stages and selecting suitable conditions for each stage. With this in view, we reacted hexamethylene iodide with sodium malonic ester. Our research indicated that this reaction can actually be divided into two phases, with the ζ-iodohexylmalonic ester being initially formed like the γ-bromopropylmalonic ester [3], the yield of the ζ-iodohexylmalonic ester being 33.8% of the theoretical when only the malonic ester is taken in excess. When the reaction involves 4 moles of the malonic ester, 2 moles of the hexamethylene iodide, and 1 gram atom of sodium as an alcoholate, the yield of the ζ-iodohexylmalonic ester totals 51.9% of the theoretical. We were unable to secure a higher yield, since the quantity of hexamethylene iodide at our disposal was too small, but there is no doubt that a higher yield can be obtained by employing a large excess of the hexamethylene iodide. Octane-1,1,8,8-tetracarboxylic ester is formed as a by-product of the reaction.

The second phase of the reaction—the conversion of the ζ-iodohexylmalonic ester into cycloheptane-1,1-dicarboxylic ester by using the customary concentrated solution of sodium alcoholate—furnishes a negligible yield, totaling 3% of the theoretical in our experiments. Thus, the seven-membered ring differs from the four-membered one in being much harder to produce than the latter.

To increase the yield of the cycloheptane-1,1-dicarboxylic ester, we made use of the assertions in the literature that a low reagent concentration was a factor that promoted ring formation.

As we know, this is the principle underlying the Ziegler method of producing compounds with higher ring systems [6]. We therefore reacted the ζ-iodohexylmalonic ester thenceforth with sodium alcoholate in a 0.1-molar solution (an alcohol-benzene mixture), and actually secured cycloheptane-1,1-dicarboxylic ester with a fairly satisfactory yield of 34.7% of the theoretical. Saponifying the cyclopentane-1,1-dicarboxylic ester yielded 93% of the theoretical quantity of cycloheptane-1,1-dicarboxylic acid, which was then converted into cycloheptane carboxylic acid, identical with that described previously [5, 7].

EXPERIMENTAL

The initial substance used in our research was hexamethylene iodide, which we prepared by reacting 1,6-diphenoxyhexane with strong hydriodic acid. 1335 g of trimethylene bromide, freed of propylene bromide by the Gustavson method [8] (b.p. 162-162.5° at 706 mm, d_{21}^{21} 1.9736, n_D^{21} 1.5215, MR_D 31.19, calculated 31.58). yielded 985 g of γ-phenoxybromopropane, with a b.p. of 113-115° at 5 mm.

Reacting an alcoholic solution of the latter with NaI yielded 1084 g of γ-phenoxyiodopropane (b.p. 135-138° at 7 mm), which was then converted into 1,6-diphenoxyhexane by the Würtz method; we made extensive use of the directions contained in the paper by Magidson Madaeva, and Rubtsov [10]. We secured a total of 220 g of diphenoxyhexane, with a m.p. of 81-83° (from alcohol or benzene).

Diphenoxyhexane is usually converted into hexamethylene iodide by heating it with fuming hydriodic acid in sealed ampoules [11]. It is much simpler, however, to prepare hexamethylene iodide by boiling 1,6-diphenoxyhexane with hydriodidic acid. We refluxed 60 g of diphenoxyhexane with 240 ml of hydriodic acid (sp. gr. 1.76) for 16-20 hours, after which we diluted the liquid with water, separated the lower layer, washed it with alkali and with water, dried it with calcined calcium chloride, and fractionated it in vacuo. This yielded an average of 48 g of a substance that boiled at 135-138° and 6 mm. A crystalline residue was left in the flask. 220 g of diphenoxyhexane yielded 176 g of hexamethylene iodide and 42 g of residue. Reboiling the latter with HI yielded another 39 g of hexamethylene iodide, the total yield being 78.1% of the theoretical.

ζ-Iodohexylmalonic ester. 100 g (0.6 mole) of malonic ester was added to a solution of the alcoholate, prepared from 3.5 g (0.15 gram atom) of sodium and 50 ml of absolute alcohol, after which 100 g (0.3 mole) of hexamethylene iodide was added. After the spontaneous heating had ceased, the reaction mixture was boiled on a bath for 6 hours. After it had cooled, water was added to the flask, the reaction products were extracted with ether, the ether extract was washed with water and a weak hyposulfite solution and dried with calcium chloride, the ether was driven off, and the residue was fractionated in vacuo. This yielded 77.3 g on the average of malonic ester fraction up to 75° at 5 mm, 48 g of hexamethylene iodide (b.p. 125-135° at 3 mm), and 40 g of a fraction with a b.p. of 150-176° at 3 mm. The distillation residue weighed 7.5 g.

Redistillation of the combined 150-176° fractions from three runs yielded 90 g of ζ-iodohexylmalonic ester, which had a b.p. of 169-170° (2.5 mm). The yield was 51.9% of the theoretical.

d_4^{20} 1.3433; n_D^{20} 1.4839; MR_D 78.78; calculated 78.34.

0.2675 g substance: 0.4078 g CO_2; 0.1444 g H_2O. 0.4682 g substance 0.3012 g AgI (by Carius method). Found %: C 41.56; H 6.00; I 34.77. $C_{13}H_{23}O_4I$. Calculated %: C 42.16; H 6.21; I 34.32.

Redistillation in vacuo of the residues of the first distillation yielded the principal fraction, with a b.p. of 226-228° at 7 mm, which was the ester of octane-1,1,8,8-tetracarboxylic acid.

d_4^{20} 1.0591; n_D^{20} 1.4473; MR_D 101.47; calculated 101.18.

0.2552 g substance: 0.5553 g CO_2; 0.1958 g H_2O. Found %: C 59.35; H 8.52. $C_{16}H_{26}O_8$. Calculated %: C 59.70; H 8.45.

This fraction was saponified with an alcoholic KOH solution, the resulting octane-1,1,8,8-tetracarboxylic acid being decarboxylated in a bath at 220-230°, converting it into sebacic acid, with a m.p. of 130-131° after recrystallization from benzene [12]. In other runs, in which no excess of hexamethylene iodide was used, an average of 18.8 g of ζ-iodohexylmalonic ester was secured from 100 g (0.6 mole) of malonic ester, 50 g (0.15 mole) of hexamethylene iodide, and 3.5 g (0.15 gram atom) of metallic sodium. In this case the yield totaled 33.8% of the theoretical.

Cycloheptane-1,1-dicarboxylic ester. 1.3 g of metallic sodium was dissolved in 25 ml of absolute alcohol, 475 ml of anhydrous benzene was added to the alcoholate solution, and then 18.5 g (0.05 mole) of ζ-iodohexylmalonic ester was added. The mixture was refluxed on a water bath for 20 hours, after which as much as possible of the benzene and alcohol was driven off, and water acidulated with sulfuric acid was added to the residue; the resultant oil was extracted with ether, the ether extract was washed with a hyposulfite solution and then with water and dried with calcined calcium chloride, and the ether was driven off, together with the residual benzene, on an oil bath (bath temperature up to 130°). The residue was distilled in vacuo, 5 g of a fraction boiling up to 145 mm at 8 mm being collected. A fairly large amount of a thick, dark oil was left in the flask.

The combined distillates of three runs were redistilled in vacuo with a dephlegmator, yielding 12.6 g of a substance that boiled at 118-121° at 4 mm (8.4 g passed over at 119°). The yield was 34.7% of the theoretical.

d_4^{20} 1.0402; n_D^{20} 1.4558; MR_D 63.21; calculated 63.34.

0.1433 g substance: 0.3377 g CO_2; 0.1654 g H_2O. Found %: C 64.27; H 9.22. $C_{12}H_{22}O_4$. Calculated %: C 64.47; H 9.09.

The substance had a faint fragrance that reminded one of the odor of cyclobutane-1,1-dicarboxylic ester. It behaved like an unsaturated compound when acted upon by a permanganate solution.

Cycloheptane-1,1-dicarboxylic acid. 10.5 g of the ester of cycloheptane-1,1-dicarboxylic acid was saponified for 1.5 hours with a 20% water-alcohol solution of potassium hydroxide, after which the liquid was diluted with water, and the alcohol driven off. After the residue had cooled it was diluted with sulfuric acid, the cycloheptane-1,1-dicarboxylic acid, which was slightly soluble in water, separating as a crystalline precipitate. The latter was suction-filtered, washed with cold water, and dried in a desiccator.

The substance had a m.p. of 177-178° after recrystallization from water. The yield was 7.5 g, or 92.9% of the theoretical.

0.1447 g substance: 0.3085 g CO_2; 0.1016 g H_2O. Found %: C 58.14; H 7.80. $C_9H_{14}O_4$. Calculated %: C 58.06; H 7.53.

The acid is slightly soluble in cold water, and more soluble in alcohol or ether. Its silver salt is a crystalline precipitate thrown down when a solution of $AgNO_3$ is added to a neutralized solution of the acid.

7 g of dried cycloheptane-1,1-dicarboxylic acid was refluxed for 6 hours at 225-230° on an oil bath. The liquid acid remaining in the flask was distilled from a Würtz flask at 245-248° (711 mm). The yield totaled 4.2 g, or 78.6% of the theoretical. The literature gives the b.p. of cycloheptanecarboxylic acid as 248-250°.

d_4^{20} 1.0368; n_D^{20} 1.4722; MR_D 38.36; calculated 38.48.

According to N. D. Zelinsky [7], cycloheptanecarboxylic acid has d_4^{17} 1.0354 and n_D^{17} 1.4710.

0.2779 g substance: 0.6842 g CO_2; 0.2496 g H_2O. Found %: C 67.15; H 9.98. $C_9H_{14}O_2$. Calculated %: C 67.60; H 9.86.

The acid was converted into an acid chloride by the action of phosphorus pentachloride, the acid chloride being added drop by drop to a chilled and concentrated solution of ammonia. The resultant amide had a m.p. of 193-194° after double recrystallization from dilute alcohol [5,7].

SUMMARY

1. ζ-Iodohexylmalonic ester has been synthesized by reacting hexamethylene iodide with sodium malonic ester.

2. Cyclization of ζ-iodomalonic ester by reacting it with sodium alcoholate in a 0.1-molar solution yielded cycloheptane-1,1-dicarboxylic ester, the yield being 34.7% of the theoretical.

3. Saponifying cycloheptane-1,1-dicarboxylic ester yielded cycloheptane-1, 1-dicarboxylic acid, which was decarboxylated to cycloheptanecarboxylic acid, identical with the acid previously described.

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Stavropol Institute of Medicine

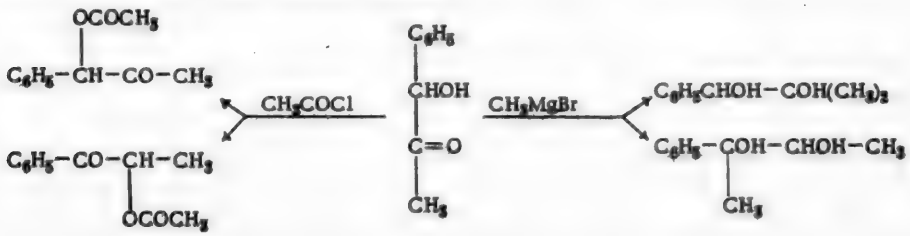
RESEARCH ON THE ISOMERIC TRANSFORMATIONS OF α-KETOLS

X. BENZYLACETYLCARBINOL

T.I.Temnikova and V.A.Kropachev

In 1934 A.E.Favorsky and T.I.Temnikova [1] discovered the extraordinary dynamicity of aliphatic-aromatic α-ketols, the example they investigated having been phenylacetylcarbinol.

They showed that when this carbinol was reacted with organomagnesium compounds and acid chlorides, the formation of the normal reaction products was paralleled by the formation of products whose structure was that of the isomeric ketol – methylbenzoylcarbinol.



In a series of papers that were a continuation of this research, it was shown that these properties occur particularly strikingly when the ketol contains a secondary alcoholic group alongside the aromatic ring and the acetyl group [2].

These peculiarities were not observed in the researches of A.E.Favorsky and his co-workers on diverse aliphatic ketols [3].

We were interested in learning how the C_6H_5 group affects the chemical properties of the ketocarbinol group, and, with this in view, in making a study of the behavior of an aliphatic-aromatic ketol whose C_6H_5 group is separated from the CHOH-CO-group by at least one carbon atom in these same reactions. The present paper is a report on our research on benzylacetylcarbinol (I), which can be readily prepared by the method described in a previous paper [4].

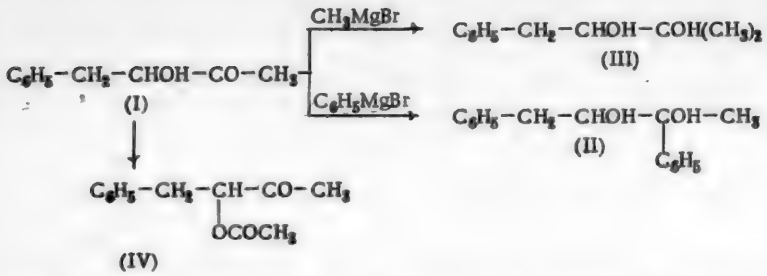
Our experiments have indicated that the reaction is normal when either C_6H_5MgBr or CH_3MgBr is used, the respective glycols: 1,3-diphenylbutanediol-2,3 (II), with a m.p. of 108-109°, and 4-phenyl-2-methylbutanediol-2,3 (III), with a m.p. of 63-64°, being produced.

The synthesis of the first glycol has been described in a previous paper [4]. The structure of the glycol, synthesized by reacting benzylacetylcarbinol with methylmagnesium bromide, was established by oxidizing it with lead tetraacetate. Phenylacetaldehyde was identified as its semicarbazone, with a m.p. of 151-152°, acetone being identified as its p-nitrophenylhydrazone. 4-Phenyl-2-methylbutanediol had been described earlier by Lévy [5], who synthesized it by reacting the ethyl ester of α-hydroxy-β-phenylpropionic acid with methylmagnesium bromide and gave its m.p. as 64-65°.

The reaction of benzylacetylcarbinol with acetyl chloride was equally normal, yielding the acetic ether of benzylacetylcarbinol (IV): (see top of next page).

Thus benzylacetylcarbinol behaves like an aliphatic ketol in the foregoing reactions, in contrast to phenylacetylcarbinol.

In our previous papers we advanced hypothetical schemas for the mechanisms involved in the processes leading to the formation of anomalous reaction products. We see from the present research that introducing a methylene group between the phenyl ring and the ketol group completely annihilated the specific influence of the phenyl



upon the mobility of the carbinol hydrogen, which is transferred during the reaction, together with an electron pair, to the adjacent carbon atom of the carbonyl group. Apparently, it is the mobility of the hydrogen atom that is the basic factor governing the rearrangement of the molecule during its reaction with acid chlorides and organomagnesium compounds. It is worthy of note that in the molecular rearrangements of the bromoketones, occurring when the bromine in bromoketones is replaced by an acetoxy group and resulting in the formation of acetic ethers of the isomeric ketols, one of the factors determining the reconstruction during the reaction is also the mobility of the hydrogen atom in the α-position to the phenyl ring, as has been demonstrated in the researches of V.I.Veksler [6].

Benzylacetylcarbinol is a stable compound, no isomeric conversion to methylphenacetylcarbinol being observed when it is heated in alcoholic solution with a few drops of H_2SO_4 or when it is acted upon by alkalies in the cold. Thus here, too, benzylacetylcarbinol behaves like a representative aliphatic ketol, for which A.E.Favorsky [3] established the rule of the high stability of isomers that contain an acetyl group.

EXPERIMENTAL

The benzylacetylcarbinol was prepared by hydrogenating benzalacetone oxide over Pd/Ni [4].

1. Reaction of benzylacetylcarbinol with methylmagnesium bromide (synthesis of 2-methyl-4-phenylbutanediol-2,3). A solution of 5 g of benzylacetylcarbinol in 30 ml of ether was added to an ether solution of methylmagnesium bromide, prepared from 3 g of magnesium. The mixture was set aside for 24 hours, after which the organomagnesium complex was decomposed with water without any acid being added. After the ether had been driven off, the colorless solid residue was recrystallized from petroleum ether; this yielded minute white crystals, shaped like pointed feathers. M.p. 63-64°. Yield: 4.4 g (80%).

0.1062 g substance: 0.2846 g CO_2; 0.0688 g H_2O. 0.1178 g substance: 0.3159 g CO_2; 0.0766 g H_2O. 0.0783 g substance: 17.2 g benzene; Δt 0.134°; 0.0738 g substance: 129 ml CH_4 (19.5°; 759.5 mm). 0.0661 g substance: 17.6 ml CH_4 (19.5°; 759.5 mm). Found %: C 73.13, 73.18; H 7.25, 7.18. M 174.3; active H 1.97, 1.94. $C_{11}H_{16}O_2$. Calculated %: C 73.29; H 7.11; M 180.13; active H 2.00.

Oxidation of the glycol with lead tetraacetate. 7 g of lead tetraacetate was added to 1.5 g of the glycol dissolved in 18 ml of glacial acetic acid, and the mixture was heated to 55°. When the crystals of lead tetraacetate had disappeared, heating was stopped, and a saturated solution of K_2CO_3 (50% of what would be required to neutralize the acetic acid) was slowly added to the cooled mass. The oxidation products were driven off with steam to identify them; the first portion of the distillate, collected in a solution of p-nitrophenylhydrazine, yielded a yellow crystalline precipitate. The crystals had a m.p. of 146-147° after recrystallization, which is the figure given for the p-nitrophenylhydrazone of acetone (the mixed melting point with a known sample exhibited no change).

As distillation was continued, yellowish drops passed over together with the steam. The distillate was collected in a semicarbazide solution, the reaction with semicarbazide being instantaneous. The m.p. of the crystals was 151-152° after they had been recrystallized from dilute alcohol. The mixed melting point with a known preparation of the semicarbazone of phenylacetaldehyde exhibited no depression. Acetone was recovered from the semicarbazide mother liquor in the usual manner and identified as its p-nitrophenylhydrazone.

In this case, therefore, we have been able to identify phenylacetaldehyde by oxidizing a glycol with a benzyl radical; in the previous experiments [4,7], apparently, the aldehyde was polymerized when the oxidation products were distilled from an alkaline medium, though they are fairly stable in an acid medium.

2. Reaction of benzylacetylcarbinol with acetyl chloride (synthesis of the acetic ether of benzylacetylcarbinol). A solution of 2.4 g of the ketol in 15 g of pyridine was chilled to 0° and 2 g of acetyl chloride (a 70% excess) was added. The mixture was set aside overnight, after which it was poured into 80 ml of 10% H_2SO_4. An oily layer was formed, which was extracted with ether. After drying with $CaCl_2$ and driving off the ether, the residue

was distilled in vacuo, all of the substance passing over, except for a few drops, at 107-108° and 1 mm. The yield was 78%. The colorless liquid reduced Fehling's solution when boiled with it.

d_4^{20} 1.0833; n^{20} 1.5000; MR_D 55.96. Calculated 55.68.

0.1116 g substance; 0.2853 g CO_2; 0.0704 g H_2O. 0.1279 g substance: 0.3267 g CO_2; 0.0799 g H_2O.

Found %: C 69.77, 69.73; H 7.06, 6.99. $C_{12}H_{14}O_3$. Calculated %: C 19.87; H 6.85.

The synthesized acetic ether was converted into a glycol to establish the structure and individuality of the substance.

An ether solution of 2.8 g of the acetyl derivative was added drop by drop, with stirring and chilling, to an ether solution of methylmagnesium bromide, prepared from 1.9 g of Mg. The rest of the processing was the usual one. This resulted in the recovery of a crystalline substance with a m.p. of 63-64°, whose mixed melting point with the glycol with a m.p. of 63-64°, synthesized from benzylacetylcarbinol and CH_3MgBr, exhibited no depression. The glycol with a m.p. of 63-64° was the sole reaction product.

3. Endeavors to isomerize benzylacetylcarbinol in an acid and an alkaline medium were made in the usual manner [2,3]. In both cases the substance recovered was converted into a glycol by reacting it with C_6H_5MgBr, a single product, with a m.p. of 108-109° being isolated, which exhibited no depression with the known glycol possessing the same melting point, prepared from benzylacetylcarbinol—1,3-diphenylbutanediol-2,3.

SUMMARY

1. It has been shown that the reaction of benzylacetylcarbinol with methylmagnesium bromide yields only a single glycol — 2-methyl-4-phenylbutanediol-2,3, which has the same structure as the initial ketol. The only product of the reaction between benzylacetylcarbinol and acetyl chloride is an acetic ether corresponding to the initial ketol.

2. Benzylacetylcarbinol has been used to define more precisely the influence of the phenyl group upon the properties of the ketocarbinol group, and it has been shown that introducing a methylene group between the phenyl and the CHOH-CO group nullifies the specific influence of the aromatic ring upon the mobility of the hydrogen atom in the carbinol group that has been observed in research upon a number of aliphatic—aromatic ketols that have aryl groups directly adjacent to the ketol group.

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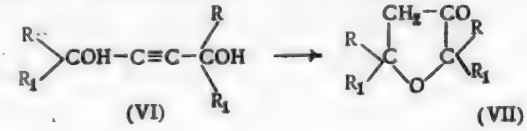
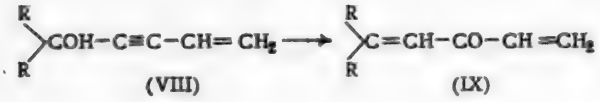
The A.E.Favorsky Laboratory of Organic Chemistry,
The A.A.Zhdanov State University of Leningrad,
Awarded the Order of Lenin

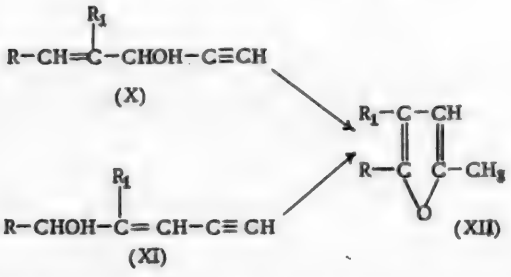
The acetylenic γ-glycols (VI), for instance, are converted into substitution derivatives of ketohydrofuran (VII) [4]; vinylacetylenic alcohols (VIII) are converted into divinyl ketones (IX) [5]; and some ene-yne alcohols (X, XI) are isomerized to substitution derivatives of furan (XII) [6]:



(VI) (VII)



(VIII) (IX)

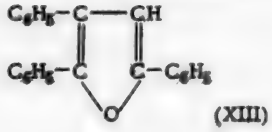


(X) (XII) (XI)

In the light of these findings, we resolved to investigate the behavior of secondary–tertiary acetylenic α-glycols (V) with mercury salts.

The first reaction we selected for this purpose was that of diphenyl phenylethynyl ethylene glycol and mercuric chloride.

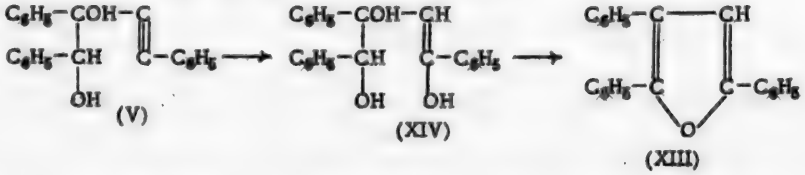
The diphenyl phenylethynyl ethylene glycol was synthesized by the Iotsich method under the conditions employed by Yu. S. Zalkind and E. E. Martinson [7], starting out with benzoin and phenylethynylmagnesium bromide. Heating the glycol with an alcoholic solution of mercuric chloride yielded 80% of a white crystalline substance with a m.p. of 91°, which proved upon analysis and from its properties to be the 2,3,5-triphenylfuran (XIII) described in the literature [8]:



(XIII)

The conversions of secondary–tertiary acetylenic α-glycols into substitution derivatives of furan by the action of mercury salts has not been described in the literature. As has been noted, however, there are reports [6] of the isomerization of unsaturated alcohols that contain both ethylenic and acetylenic bonds into substitution derivatives of furan when they are heated with mercuric sulfate or mercuric oxide and boron trifluoride in methanol.

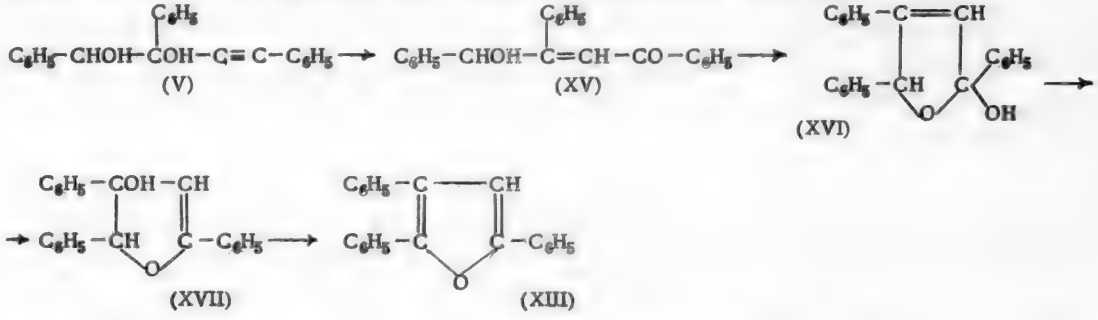
As for the mechanism of this transformation, it is simplest to assume that it involves the partial hydration of the acetylenic bond of the secondary–tertiary glycol (V) and the formation of the trihydroxy compound (XIV), which loses two molecules of water and turns into 2,3,5-triphenylfuran (XIII):



(V) (XIV) (XIII)

This is how A.E.Favorsky conceived of the conversion of diphenyl phenylethynyl ethylene glycol into 2,3,5-triphenylfuran in 1915 [9], though he did not indicate the reaction conditions and merely referred to unpublished research by N.V. Palladin.

But in view of the mobility of the hydroxyl group at the α-position to the triple bond [10] and the ability of ditertiary acetylenic α-glycols to enter into an acetylenic–allenic rearrangement [11,2,3], which A.N.Elizarova and I.N.Nazarov [5] believe can also be effected by mercury salts, we may state that in our case the furan compound was formed from the unsaturated secondary γ-ketol (XV) via the hydroxyhydrofuran (XVI), which is converted into a substitution derivative of furan as the result of an allylic rearrangement (XVII) and dehydration:



This reaction will have to be checked for other glycols of analogous structure, and their behavior toward sulfuric acid to determine the feasibility of an acetylenic–allenic rearrangement for them, if we are to obtain a final solution of the problem of the way in which 2,3,5-triphenylfuran is produced from diphenyl phenylethynyl ethylene glycol.

EXPERIMENTAL

I. Synthesis of Diphenyl Phenylethynyl Ethylene Glycol (1,2,4-Triphenyl-butyn-3-diol-1,2)

According to the literature [7], the glycol was synthesized from phenylacetylene, magnesium, and benzoin, its m.p. being 175° after recrystallization from benzene and then from ethyl alcohol. The yield was 58%, based on the benzoin used. Neither the melting point of the glycol nor its properties differed from those of the diphenyl phenylethynyl ethylene glycol described in the literature.

II. Action of Mercuric Chloride upon Diphenyl-Phenylethynyl Ethylene Glycol

Experiment 1. A saturated alcoholic solution of the glycol (1 g of the glycol in 15 ml of 96% ethyl alcohol), to which 0.3 g of mercuric chloride had been added, was heated for 8 hours in a sealed tube on a boiling water bath. A yellowish mass formed at the bottom of the tube, the alcoholic solution being threaded through by a white crystalline substance. The amorphous mass was separated, washed twice with hot water to remove the mercuric chloride, and recrystallized from alcohol. This yielded 0.2 g of a finely crystalline white powder with a m.p. of 89°. 0.6 g of a white crystalline product was filtered out of the alcoholic layer; its m.p. was 90° and it exhibited no depression of the mixed melting point with the substance whose m.p. was 89°, which had been isolated from the deposit on the bottom of the tube.

Experiment 2. A saturated alcoholic solution of the glycol (1 g of the glycol in 15 ml of ethyl alcohol), containing 0.6 g of mercuric chloride, was heated for 8 hours in a sealed tube on a boiling water bath. As in Experiment 1, we secured 0.15 g of a substance with a m.p. of 89° and 0.7 g of a substance with a m.p. of 90°, suspended in the alcohol.

Experiment 3. 0.9 g of mercuric chloride and a saturated alcoholic solution of the glycol (1 g of the glycol in 15 ml of 96% ethyl alcohol) were heated together for 6 hours in a sealed tube at 110-115°. This yielded a white crystalline substance, which filled the entire tube. The substance weighed 0.85 g and had a m.p. of 91° after washing with hot water and recrystallization from alcohol.

The experimental results are summarized in the following table:

Test No.	Glycol (g)	Mercuric chloride, g	Heating time, hrs	Heating temp.	Yield g	Yield %
1	1	0.3	8	100°	0.8	85.1
2	1	0.6	8	100°	0.85	90.4
3	1	0.9	6	110-115	0.85	90.4
	3	1.8			2.5	88.6

We see that the product yield is unaffected by any change in the amount of mercuric chloride used, the heating time, or the temperature. A total of 2.5 g of the substance was secured, its m.p. being 91° after another recrystallization.

The substance with a m.p. of 91° is freely soluble

in ether and benzene, but less so in alcohol. It decolorizes a chloroform solution of bromine and an aqueous solution of potassium permanganate when heated in them; it contains neither a hydroxyl nor a carbonyl group; and it colors strong sulfuric acid a deep red, the color disappearing when the acid is diluted with water.

0.1037 g substance: 0.3386 g CO_2; 0.0510 g H_2O. Found, %: C 89.05; H 5.46. $C_{22}H_{16}O$. Calculated %: C 89.19; H 5.40. 0.1051 g substance: 12.96 g C_6H_6: Δt 0.14°. Found: M 281. $C_{21}H_{16}O$. Calc.: M 296.

Analysis and the properties of the substance with a m.p. of 91° indicate that it is 2,3,5-triphenylfuran, whose m.p. is given in the literature as 92° [8]. The yield was 88.6%.

This substance is the sole product of the transformation of diphenyl phenylethynyl ethylene glycol when acted upon by mercuric chloride.

SUMMARY

When an alcoholic solution of mercuric chloride is reacted with diphenyl phenylethynyl ethylene glycol at 100°, 2,3,5-triphenylfuran is produced the yield being 88.6%.

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Laboratory of Organic Chemistry,
The Lensoviet Institute of Technology, Leningrad

INVESTIGATION OF THE ABSORPTION SPECTRA OF SOME DI- AND TRIPHENYLMETHANE DERIVATIVES

V. V. Perekalin, M. V. Savostyanova, and R. I. Morozova

In our research on the absorption spectra of some derivatives of naphthalene and of the azo dyes synthesized from these derivatives, we discovered that the absorption bands of the initial products are repeated, with a few deviations, in the spectra of the azo dyes [1]. With a view to confirming and extending this observation, we have investigated, for the first time, the absorption spectra of 15 genetically interrelated di- and tri-phenylmethane compounds (intermediates and dyes*) over a wide wavelength range (210-650 mμ). We were also interested in tracing the ways in which the absorption spectra evolve when the structure of a substance is changed.

The spectrophotometric measurements were made with a Type SF-1 photoelectric device; the effective slit width was about 1 mμ at 250 mμ. This enabled us to resolve the fine structure of the absorption bands whenever the distances between maxima were of that order of magnitude. The absorption of the solvent has been excluded from all our findings. With the sole exception of dimethylaniline, all the substances were specially synthesized and thoroughly purified (recrystallization from various solvents and distillation in vacuo). Identical concentrations were used in our research, these concentrations being later recalculated into molar concentrations (C_m); the same solvent (ethyl alcohol; pH = 8) was employed in every case, as a rule. The absorption spectra were measured for freshly prepared solutions, as well as for the solutions after they had stood in the dark for 24 hours. The position of the bands remained constant, only their intensity changing slightly; hence, the substances were sufficiently stable under the experimental conditions we employed.

Diphenylmethane (I) [2-9] and triphenylmethane (II) [4,6,8,9-11]** were the parent substances of all the compounds tested. The absorption spectra of these substances have a single absorption band that exhibits fine structure (Figure 1). In both of these compounds, the center of gravity of each band (262 mμ), as well as the location of the fine-structure bands and their intensity ratios, coincide nearly completely.

The absorption spectra of diphenylcarbinol (III) and triphenylcarbinol (IV) [4,12-14] retain the fine structure of the absorption band. The spectra of both carbinols are pretty much alike, differing from the spectra of the respective hydrocarbons (I) and (II) in that they exhibit a decrease in the number of the fine-structure bands and a change in the intensity ratios of these bands.

Comparison of the spectra (I), (II), (III), and (IV) indicates that the substitution of a benzene ring for the hydrogen atom attached to the central carbon atom increases the intensity of the absorption band (ε), while substituting a hydroxyl group for the hydrogen atom lowers the intensity and results in widening of the elementary bands.

When two dimethylamino groups are introduced into diphenylmethane and one, two, or three dimethylamino groups into triphenylmethane, the absorption band of the initial substance is preserved in the absorption spectra of these amines, while a new, though rather weak, band, at the longer wavelength of 300 mμ distinctly makes its appearance (Figures 3 and 4, and Table 1). It should be noticed that dimethylaniline (V) [3,6,15-17] has an absorption spectrum whose band positions and intensity ratios are quite close to those of the spectra of the tested di- and triphenylmethane amines (Fig. 3, Table 1). Increasing the number of dimethylamino groups in the compounds in question does not cause any new band to appear, merely promoting the reappearance of the fine structure of the al-

* Some of the substances we have investigated have been analyzed spectroscopically more than once in the past, the results agreeing with those obtained in our research (as in di- and triphenylmethane and the triphenylmethane dyes—malachite green and crystal violet), but no systematic investigations have been carried out with the objective set forth above. There are no figures in the literature for several of these substances (VI, VII, VIII, IX, and X).

** The absorption curve rises at $\lambda < 210$ mμ in all the substances, due to the presence of a band in the 200 mμ region.

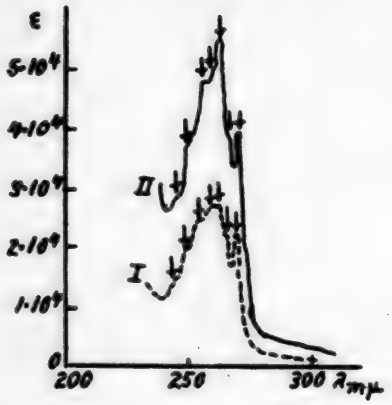


Fig. 1. Absorption spectra: I) diphenylmethane; II) triphenylmethane.

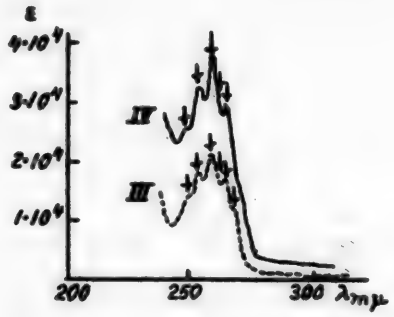


Fig. 2. Absorption spectra: III) diphenylcarbinol; IV) triphenylcarbinol

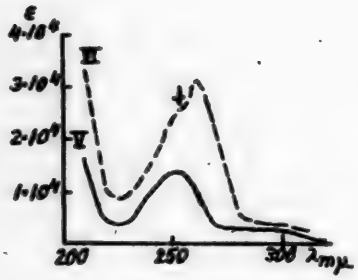


Fig. 3. Absorption spectra: V) di-m-phenylaniline; VI) tridiaminodiphenylmethane.

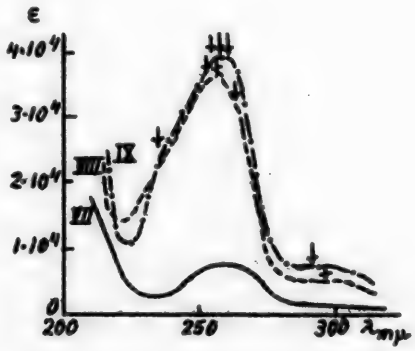


Fig. 4. Absorption spectra: VII) Dimethyldiaminotriphenylmethane; VIII) leucomalachite green; IX) leucocrystal violet.

ready existing shortwave band, which is absent in the compound (VII) and distinctly visible in (IX), and increasing the intensity of both absorption bands [compare spectra (VII), (VIII), and (IX).]

The intensity ratios of the shortwave to the longwave bands diminishes in that order; however, the growth of the shortwave band outstripping that of the longwave one.

The carbinol derivatives of part of the amines discussed above exhibit optical properties that are unexpectedly somewhat different from those of the amines proper. To be sure, the spectra of the carbinols (X), (XI), and (XII) [13] (Figure 3 and Table 1)[(XI) and (XII) are the carbinol bases of malachite green and crystal violet], like those of the initial amines, retain two absorption bands at the same wavelengths; the transition from the diphenylmethane carbinols to the triphenylmethane carbinols and an increase in the latter's dimethylamino groups, however, cause a decrease rather than an increase in the intensity of both bands, to begin with, and second, does not cause a more distinct manifestation of the fine structure of the shortwave band, as was the case with the amines.

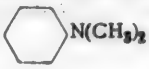
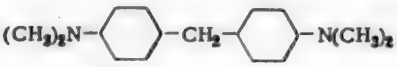
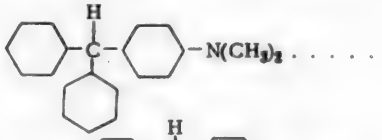
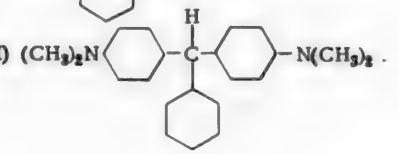
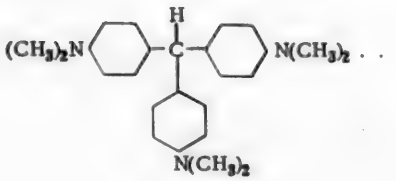
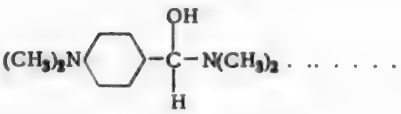
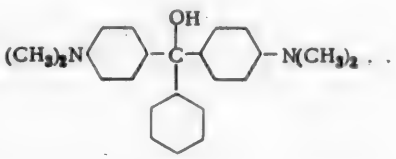
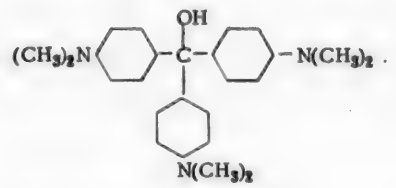
Thus, the absorption spectra of the investigated di- and triphenylmethane hydrocarbons [di- and triphenylmethane, (I) and (II)] and their hydroxyl derivatives [di- and triphenylcarbinol, (III) and (IV)] have one distinct absorption band that possesses fine structure. The introduction of dimethylamino groups into these compounds preserves this shortwave band in the spectra of the resultant substances (the fine structure of the band being obliterated) and results in the appearance of a weak new band at longer wavelengths.

This picture grows much more complicated when we explore the absorption spectra of colored salts or dyes, derived from the intermediates mentioned above.

The spectrum of the colored salt of tetramethyldiaminodiphenylmethane (XIII) [18,19], prepared from the carbinol (X), retains both bands of the original carbinol; moreover, a new low intensity band appears in the longwave region of the spectrum (Figure 6 and Table 2).

Malachite green (XIV) [13, 19-22] was tested at pH values that made hydrolysis impossible [23], resulting in the formation of an equilibrium mixture of the dye and the carbinol; thus what we measured was a solution of the dye proper.

TABLE 1

Substance*	C_m	I		II		
		λ	$\varepsilon \cdot 10^{-4}$	λ	$\varepsilon \cdot 10^{-4}$	$\frac{\varepsilon_1}{\varepsilon_2}$
(V) 	–	251	1.34	290	0.25	5.3
(VI) 	$7.8 \cdot 10^{-5}$	(255) 262	(2.6)** 3	300	0.42	7.1
(VII) 	$6.1 \cdot 10^{-5}$	260	0.73	300	0.094	7.7
(VIII) 	$6.0 \cdot 10^{-5}$	(260) 262 (268)	(3.47) 3.52 (3.2)	300	0.53	6.6
(IX) 	$5.3 \cdot 10^{-5}$	(240) 260.0 262.5 265.0	(2.32) 3.78 3.84 3.82	298	0.74	5.1
(X) 	$7.4 \cdot 10^{-5}$	267	2.48	300	0.33	–
(XI) 	$5.8 \cdot 10^{-5}$	(260) 264	(1.4) 1.58	300	0.2	–
(XII) 	$5.0 \cdot 10^{-5}$	260	0.24	300	0.11	–

* Spectra (V) through (IX) were explored in ethyl alcohol mixed with a few drops of a 10% hyposulfite solution; (X) was explored in ethyl alcohol, pH = 8.0; (XI) and (XII) in an alcoholic–alkaline medium, pH = 12.0, the alkali being added until dissociation of the carbinols was prevented, resulting in formation of the colored dye ion.

** The figures for weak maxima are given in parentheses.

The spectrum of malachite green (Figure 7 and Table 2) retains both of the shortwave bands in the spectrum of the leuco and carbinol bases (VIII) and (IX) from which it can be produced. But the dye exhibits some displacement of the shortwave band toward the ultraviolet, compared to the spectra of these substances, while the longwave band is displaced toward the visible region; we discovered a redistribution of the intensities of these bands: the intensity of the shortest wavelength band dropped markedly, while that of the longer wavelength band rose considerably (Table 3); what is more, two new bands appeared in the visible region of the dye's spectrum.

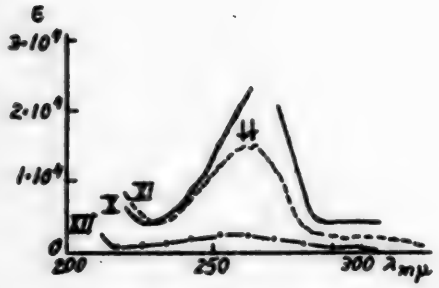


Fig. 5. Absorption spectra: X) tetramethyldiaminodiphenylcarbinol; XI) carbinol base of malachite green; XII) carbinol base of crystal violet.

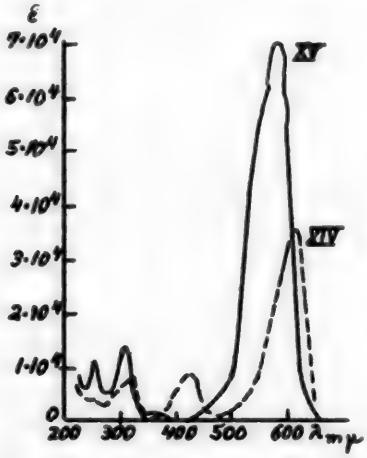


Fig. 7. Absorption spectra: XIV) malachite green; XV) crystal violet.

Another triphenylmethane dye, crystal violet (XV) (Fig. 7 and Table 2) [13, 19-21], which was also tested at a pH that excluded the possibility of any hydrolysis of the dye, retains in its spectrum the two shortwave bands of the leuco and carbinol bases; the intensities of these bands are redistributed as was the case with malachite green (Table 3), though to a lesser extent; there is a very weak band at the edge of the visible region, which is followed by the strong band of the dye proper. The fine structure of the shortwave band has vanished completely in the spectra of both dyes.

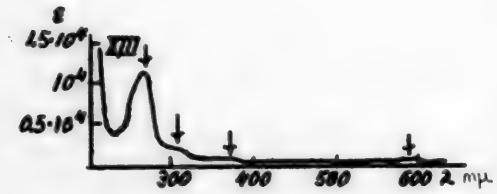


Fig. 6. Absorption spectra: XIII) salt of tetramethyldiaminodiphenylcarbinol.

We then tried to track down the genesis of the second absorption band of malachite green, located in the visible region (λ = 425 mμ). We did this by investigating the absorption of the dihydrochloride of malachite green (XIVa) [13,24] and the trihydrochloride of crystal violet (XVa) [25], which were prepared by dissolving the dyes in concentrated hydrochloric acid, which made hydrolysis of these salts highly unlikely. In the absorption spectrum of the salt (XIVa) only the band of the original dye located at the longest wavelength disappears, the positions of the other three bands, at shorter wavelengths, suffering no substantial changes; merely the longest wavelength band of the salt is shifted toward the visible region (λ = 442 mμ), compared to the corresponding band in the dye. Lastly, the intensity of the whole spectrum drops sharply (Figure 8 and Table 4).

In the spectrum of the salt (XVa) the longwave band of crystal violet also vanishes, together with the weak band located at the boundary of the visible region (λ = 360 mμ).* At the same time, a new band arises in the visible region (λ = 435 mμ); the other two shortwave bands retain their position (Figure 8 and Table 4).

* The disappearance of this band when a salt of crystal violet is formed disproves the assumption of its common origin with the intermediate band of malachite green and the longwave band of diaminotriphenylcarbinol (XVI).

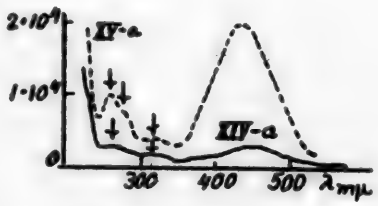
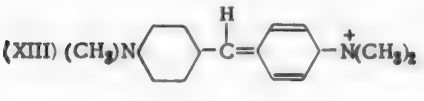
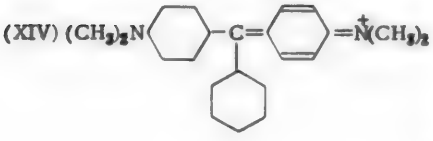
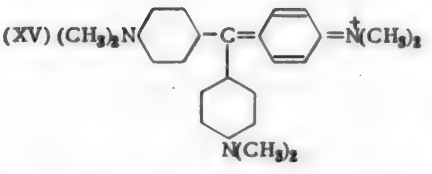


Fig. 8. Absorption spectra: XIVa) malachite green dihydrochloride; XVa) crystal violet trihydrochloride.

TABLE 2

Substance	Cm	pH	I		II		III		IV	
			λ	ε·10⁻⁴	λ	ε·10⁻⁴	λ	ε·10⁻⁴	λ	ε·10⁻⁴
(XIII) 	6.9·10⁻⁵	Ethyl alcohol 8.0*	265	1.14	300	6.2	(340)	(0.058)	595	0.03
(XIV) 	5.4·10⁻⁶	Buffer 4.2	249	0.35	316.5	0.82	425	0.86	620	3.44
(XV) 	4.9·10⁻⁵	Buffer 5.67	250	1.09	303	1.37	(360)	(0.13)	589 (560	6·97 5.68)

* We have been unable to select a buffer for this dye which would dissolve it completely and permit adequate transmission in the ultraviolet; hydrolysis may take place in ethyl alcohol, so that the figures given for ε are merely approximate.

TABLE 3

Intensity Ratios of Two Shortwave Absorption Bands

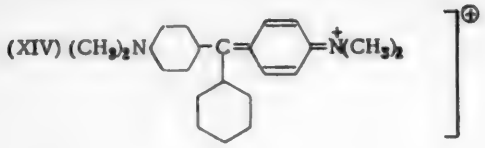
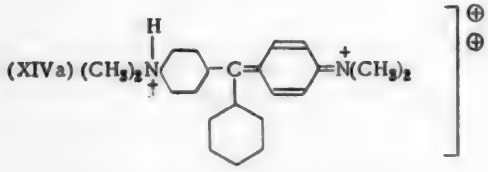
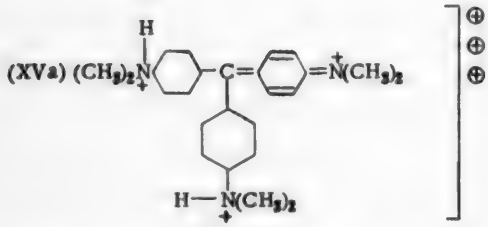
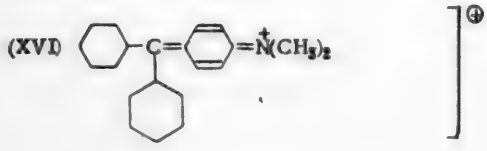
Substance	(VIII)	(XI)	(XIV)	(IX)	(XII)	(XV)
$\frac{\varepsilon_1}{\varepsilon_2}$ . . .	6.64	7.9	0.43	5.2	2.0	0.8

Formation of the malachite green dihydrochloride (XIVa) and crystal violet trihydrochloride (XVa) is accompanied by elimination of the longwave band in the spectra of the initial dyes, owing to the interaction of the dimethylamine groups of these dyes with the hydrogen ions and their conversion into groups with an electron configuration that resembles that of the optically inactive methyl group. The structure of these salts is like that of the salt of dimethylaminotriphenylcarbinol (XVI) [13,26] (Table 4), which contains one postively charged dimethylamino group, the spectrum of which we know has only one absorption band in the visible region (λ = 480 mμ), whose position is close to that of the longwave bands of salts (XIVa) and (XVa) and of the intermediate band of malachite green. The conclusion that thrusts itself upon one, therefore, is that the absorption spectrum of malachite green contains not only the bands of the leuco and carbinol bases, but also the band of the salt (XVI), which is the foundation of the dye.

Thus there is a single pattern of development of the absorption spectra that is common to all of the three genetic series constituted: 1) by the salt of tetramethyldiaminodiphenylcarbinol (XIII); 2) malachite green (XIV); and 3) crystal violet (XV), and to the salts of the last two and the respective leuco and carbinol bases of these dyes; with a few exceptions, the dye's absorption spectrum repeats the bands of the initial products; moreover, the dyes' spectra repeat only the strong absorption bands, located in the visible region as a rule, that belong to them.

Another rule observed by us appears with even greater distinctness in the absorption spectra of phenylmethylpyrazolone and its various derivatives. Phenylmethylpyrazolone exhibits in its spectrum one strong absorption band at 246 mμ; in all the compounds, without exception, that were synthesized by reacting phenylmethylpyrazolone with aldehydes, nitroso and diazo compounds (a large number of substances, some of which had highly complicated structures, was investigated [27], the absorption band of phenylmethylpyrazolone is preserved, a new band belonging to the given compound making its appearance in the longwave region, and the intensity of the shortwave band being somewhat less than that of the longwave one and lower than in the original phenylmethylpyrazolone.

TABLE 4

Substance*	I		II		III		IV	
	λ	ε·10⁻⁴	λ	ε·10⁻⁴	λ	ε·10⁻⁴	λ	ε·10⁻⁴
(XIV) 	249	0.35	316.5	0.82	425	0.86	620	3.44
(XIVa) 	262	0.25	320	0.12	442	0.275	–	–
(XVa) 	259 (280)	0.99 (0.7)	314	0.375	436	0.98	–	–
(XVI) 	250 (285)	–	333	–	480	–	–	–

* (XIVa) and (XVa) were explored in 30% hydrochloric acid, while (XVI) was explored in dilute hydrochloric acid.

The following considerations may be put forward in connection with the genesis of the absorption bands in the spectra of the substances tested. As we know, each electronic band arises as the result of a shift of the molecule from the ground state to an excited state. At that instant only a single absorption band arises in the spectrum, since the molecule can effect only a single energy change at a time. Hence the spectrum of a compound that exhibits several absorption bands is a statistical picture of various energy changes.

Whenever the location of a spectrum band of a dye (say, the shortwave band of crystal violet) coincides with that of the original compound (say, the carbinol base of crystal violet), it may be assumed that the excitation energies responsible for the appearance of these bands are the same. Hence, the energy changes of the original substances are reproduced in the dyes. The intensity of the absorption bands is determined by the probability of the energy changes.

SUMMARY

1. Investigation of the absorption spectra of numerous diphenylmethane and triphenylmethane compounds, as well as of phenylmethylpyrazolone and of various dyes synthesized from these substances shows that the absorption bands of the original substances are repeated in the spectra of the dyes.

2. It has been established that this phenomenon is accompanied by a certain shift of the position of the shortwave bands (compared to the initial products) in the dye spectra and by a redistribution of their intensities.

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DERIVATIVES OF ACETYLENE

138. HETEROCYCLIC COMPOUNDS

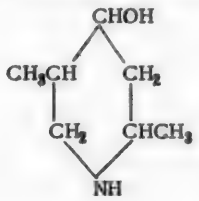
XIV. Synthesis of Secondary γ-Piperidols by Reducing γ-Piperidones

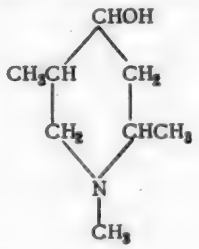
I. N. Nazarov and V. A. Rudenko

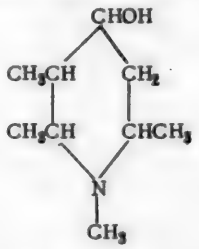
The high physiological activity of many natural esters of the secondary γ-piperidinic alcohols (cocaine, atropine, scopolamine, and the like) and of synthetic preparations of similar structure, which have been widely employed as anesthetics and mydriatics (eucaine, euphthalmine), is largely responsible for the undiminished interest in this group of compounds. The compounds of this type that have been synthesized and tested recently include substances that are highly active spasmolytically [1] and mydriatically [2], possess strong curarelike activity [3], and can be employed as substitutes for quinidine [4]. The secondary alcohols of the γ-piperidine series may also be intermediate products in the synthesis of substitution derivatives of the γ-aminopiperidines that act as spasmolytics.

We were, of course, interested in synthesizing the secondary γ-alcohols of the piperidine series by reducing the respective γ-piperidones, which have become readily available in wide variety as the result of our discovery of a simple method of producing them by reacting vinyl allyl ketones with ammonia and primary amines [5].

Reducing 2,5-dimethyl-4-piperidone with metallic sodium in absolute alcohol yielded 2,5-dimethyl-4-piperidol (I) with a m.p. of 96-97°. A Raney nickel catalyst hydrogenates 2,5-dimethyl-4-piperidol to a mixture of isomeric 2,5-dimethyl-4-piperidols, the bulk of which is the isomer (II) with a m.p. of 138°:







(I) M.p. 96-97°;
(II) M.p. 138°;

(III) B.p. 80-81° at 5 mm;
picrate m.p. 138-139°;

(IV) B.p. 87-88° at 7 mm;
picrate m.p. 116-118°.

(V) M.p. 77-79°;
picrate m.p. 181-182°.

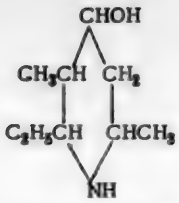
(VI) B.p. at 4 mm 92-93°;
picrate m.p. 104-106°.

Reducing 1,2,5-trimethyl-4-piperidone with metallic sodium in absolute alcohol yielded liquid 1,2,5-trimethyl-4-piperidol (III) with a b.p. (5 mm) of 80-81°; the picrate m.p. was 138-139°. Hydrogenation of 1,2,5-trimethyl-4-piperidone at room temperature with a platinum catalyst likewise yielded liquid 1,2,5-trimethyl-4-piperidol (IV) with a b.p. (7 mm) of 87-88°; the picrate m.p. was 116-118°.

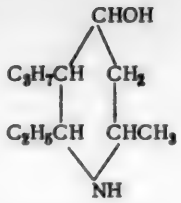
Reducing 1,2,3,6-tetramethyl-4-piperidone with metallic sodium in absolute alcohol yielded 2 isomers: a crystalline isomer with a m.p. of 77-79° (V) and a liquid isomer with a b.p. at 4 mm of 92-93° (VI). The isomeric alcohols were separated and then isolated in the pure state by fractionally crystallizing their picrates, followed by decomposing the individual picrates with a concentrated potash solution.

Reducing 2,5-dimethyl-6-ethyl-4-piperidone with metallic sodium in absolute alcohol under the same conditions likewise yielded a mixture of isomeric alcohols, from which we were able to isolate only one crystalline 2-methyl-6-ethyl-5-propyl-4-piperidol (VIII) with a m.p. of 123°, as in the previous test.

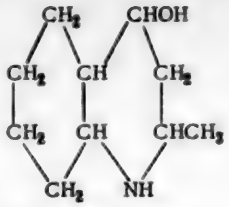
Successive fractional crystallization of the mixture of isomeric alcohols produced by reducing 2-methyl-4-ketodecahydroquinoline with metallic sodium in alcohol yielded 2 crystalline isomers of 2-methyl-4-hydroxydecahydroquinoline, with a m.p. of 111-113° (IX) and 185-186° (X):



(VII) M.p.136-137°

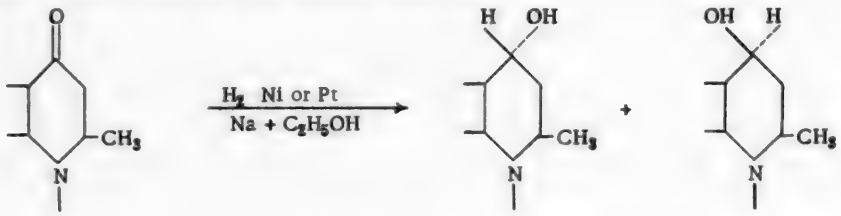


(VIII) M.p.123°



(IX) M.p. 111-113°
(X) M.p. 185-186°

Thus, whether the substitution derivatives of γ-piperidones are reduced with metallic sodium in alcohol or catalytically hydrogenated with Ni and Pt catalysts, we usually obtain a mixture of stereoisomeric γ-piperidols, their proportions varying widely with the reaction conditions:



Only in reduction of 2,5-dimethyl-4-piperidone with metallic sodium in alcohol do we get an individual 2,5-dimethyl-4-piperidol (m.p. 96-97°), every other case resulting in a complex mixture of stereoisomers, this being particularly true when the carbonyl group is reduced in γ-piperidones that contain three or more substituents attached to the piperidine ring. This indicates that the hydrogenation of substitution derivatives of the γ-piperidones not only results in the formation of a new asymmetric carbon atom at the 4 position, but also sets up a different spatial arrangement of the substituents attached to the other atoms in the piperidine ring.

EXPERIMENTAL

2,5-Dimethyl-4-piperidol. 1) 12.7 g of 2,5-dimethyl-4-piperidone (b.p. 70° at 8 mm; n_D^{12} 1.4690) was dissolved in 350 ml of absolute alcohol and 35 g of metallic sodium was added in small pieces to the solution. After all the sodium had dissolved, 100 ml of water was added to the alcoholate, and then the mixture was stirred while 150 ml of concentrated hydrochloric acid was added until the mixture's reaction was acid. After the alcohol had been driven off, the salt solution was evaporated in a pan on a water bath, the sodium chloride being filtered out while hot. The filtrate (totaling about 150 ml) was saturated with alkali and extracted four times with ether. The ether solution was dried with calcined potash. After the ether had been driven off, the residue was distilled in vacuo (b.p. 85° at 4 mm), solidifying rapidly in the receiver. This yielded 9.5 g of a low-melting isomer of 2,5-dimethyl-4-piperidol (I), which had a m.p. of 96.5-97° after recrystallization from benzene and acetone.

3.228 mg substance: 7.677 mg CO_2; 3.410 mg H_2O. 3.210 mg substance: 7.657 mg CO_2; 3.410 mg H_2O. Found %: C 64.90, 65.10; H 11.82, 11.85. $C_7H_{15}ON$. Calculated %: C 65.07; H 11.70.

The picrate of the low-melting isomer of 2,5-dimethyl-4-piperidol settled out, after part of the alcohol had been driven off, from a mixture of the base and a saturated alcoholic solution of picric acid. Yellow crystals, m.p. 176-177° (from alcohol).

The hydrochloride of 2,5-dimethyl-4-piperidol was prepared by reacting a solution of the base in absolute alcohol with anhydrous hydrogen chloride. Driving off the solvent and recrystallizing twice from alcohol yielded large crystals with a m.p. of 218-219°.

2) A solution of 12.6 g of 2,5-dimethyl-4-piperidone (b.p. 67.5° at 7 mm; n_D^{18} 1.4660) in 15 ml of alcohol was heated with 0.3 g of Raney nickel catalyst in a 156-ml autoclave under a hydrogen pressure of 148 atm. Hydrogenation set in at 90-100° and was complete after 2 hours 15 minutes. The catalyst was filtered out, the alcohol driven off, and the product distilled in vacuo. This yielded 11.5 g of a partially crystallized mixture of isomers of 2,5-dimethyl-4-piperidol, with a b.p. of 86-90° at 6 mm. The crystals were pressed out on a glass filter, washed with a small quantity of acetone, and recrystallized from acetone. This yielded 2.5 g of the high-melting 2,5-dimethyl-4-piperidol (II) as light, lustrous lamellae with a m.p. of 138°.

3.474 mg substance:)) 8.220 mg CO_2; 3.675 mg H_2O. 3.310 mg substance: 7.850 mg CO_2; 3.310 mg H_2O. Found %: C 64.67, 64.72; H 11.83, 11.86. $C_7H_{15}ON$. Calculated %: C 65.07; H 11.70.

The picrate of the high-melting isomer of 2,5-dimethyl-4-piperidol was produced by mixing alcoholic solutions of the base and of picric acid and driving off part of the solvent. M.p. 177-178° (from alcohol). The mixed melting point with the picrate of the low-melting isomer of 2,5-dimethyl-4-piperidol described above was 144-147°.

The hydrochloride of the high-melting isomer of 2,5-dimethyl-4-piperidol was prepared by reacting a solution of the base in absolute alcohol with anhydrous hydrogen chloride. Large crystals crystallized out of the solution by the following day; they were filtered out and washed with a small quantity of alcohol. M.p. 208-210°. Crystals in the shape of thin lamellae were secured from the filtrate after anhydrous ether had been added to it. Their m.p. was likewise 208-210° after washing on the filter and drying.

1,2,5-Trimethyl-4-piperidol. 1) 14.1 g of 1,2,5-trimethyl-4-piperidol (b.p. 64-65° at 8.5 mm; n_D^{21} 1.4590) was dissolved in 350 ml of absolute alcohol, and 35 g of metallic sodium was added in small pieces to the alcoholic solution. The alcoholate solution was then diluted with 100 ml of water and neutralized with 165 ml of concentrated hydrochloric acid. The sodium chloride was filtered out of the neutralized solution, the alcohol was driven off, and the remaining solution was evaporated in a porcelain dish on a water bath to a volume of some 75 ml. The action of a solid alkali caused a layer of an amino alcohol to separate; this layer was repeatedly extracted with ether, dried with alkali, and fractionated in vacuo. This yielded 9 g of a mixture of isomeric 1,2,5-trimethyl-4-piperidols (b.p. 73-82° at 6 mm; n_D^{21} 1.4720), from which we secured 4.1 g of 1,2,5-trimethyl-4-hydroxypiperidine (III) with a b.p. 80-81° at 5 mm; n_D^{20} 1.4738; d_4^{20} 0.9522; MR 42.55; calculated 42.41.

3.790 mg substance:) 0.326 ml N_2 (21° at 730 mm). 4.530 mg substance: 0.385 ml N_2 (20° at 738 mm). Found %: N 9.59, 9.61. $C_8H_{17}ON$. Calculated %: N 9.78.

The picrate was prepared by mixing together the base and an alcoholic solution of picric acid. After the solvent had been driven off, it took three weeks for the thick, dark-red mass to crystallize. The picrate had a m.p. of 138-139° (yellow crystals) after the crystalline mass had been washed with ether and recrystallized three times from alcohol.

The hydrochloride was prepared by passing a current of anhydrous hydrogen chloride through an alcoholic solution of the base. Driving off the solvent left behind an oily product. Precipitation with ether from the alcoholic solution threw down crystals together with an oily product. Heating in acetone with a small quantity of alcohol yielded crystals (m.p. 176-182°), which settled out again together with an oil when they were dissolved in alcohol and precipitated with ether. Crystals of 1,2,5-trimethyl-4-piperidol, with a m.p. of 192-194°, were isolated by fractional precipitation with ether from an alcoholic solution.

2) 13.5 g of 1,2,5-trimethyl-4-piperidone (b.p. 63-64° at 7 mm; n_D^{21} 1.4578) were hydrogenated in 30 ml of alcohol with a platinum catalyst. At the start hydrogen is absorbed rapidly, but within an hour, after 500 ml had been absorbed, absorption slowed down, taking 36 hours to be completed. A total of 2.4 liters of hydrogen was absorbed. Fractionation of the hydrogenation product in vacuo yielded 11 g of a mixture of isomeric amino alcohols (b.p. 81-88° at 7 mm), from which double fractionation yielded 8.5 g of 1,2,5-trimethyl-4-piperidol (IV) as a colorless, viscous liquid with the odor of an amine; b.p. 96-96.5° at 10 mm; 87-88° at 7 mm; n_D^{20} 1.4750; d_4^{20} 0.9549; MR 42.22; calculated 42.41.

7.67 mg substance; 18.83 mg CO_2; 8.32 mg H_2O. 8.34 mg substance: 20.42 mg CO_2; 9.13 mg H_2O. Found %: C 67.00, 66.81; H 12.14, 12.25. $C_8H_{17}ON$. Calculated %: C 67.09; H 11.96.

The picrate of 1,2,5-trimethyl-4-piperidol was prepared by mixing the base with an alcoholic solution of picric acid. Driving off the solvent yielded the crystals of the picrate, which had a m.p. of 116-118° after recrystallization from alcohol.

1,2,3,6-Tetramethyl-4-piperidol. 15.5 g of 1,2,3,6-tetramethyl-4-piperidone (b.p. 71° at 6.5 mm; n_D^{20} 1.4670) was dissolved in 350 ml of absolute alcohol, and 35 g of metallic sodium was added in small pieces to the alcoholic solution. After all the sodium had been added, the alcoholate solution was diluted with 150 ml of water and neutralized by gradually adding 165 ml of concentrated hydrochloric acid. The precipitated sodium chloride was filtered out, the alcohol was driven off from the filtrate, and the latter was evaporated to a volume of 70-90 ml in a porcelain dish on a water bath. The free base was isolated by the action of a solid alkali, extracted with ether, and dried in vacuo. This yielded 9.5 g of 1,2,3,6-tetramethyl-4-piperidol as a viscous, colorless liquid with the faint odor of an amine; b.p. 100-102° at 7 mm; n_D^{20} 1.4830; d_4^{20} 0.9626; MR 46.65; calculated 47.03.

Four days later crystals appeared on the bottom of the flask containing the reaction product, their quantity increasing slightly after the mixture had been chilled and rubbed with a rod. The crystals were filtered out on a dense glass filter and washed on the filter with a small quantity of acetone. This yielded about 0.1 g of a crystalline isomer of 1,2,3,6-tetramethyl-4-piperidol (V), with a m.p. of 77-79°, which was soluble in water, alcohol, ether, petroleum ether, acetone, carbon tetrachloride, benzene, and ligroin.

5.310 mg substance: 13.325 mg CO_2; 5.745 mg H_2O. 4.160 mg substance: 10.400 mg CO_2; 4.480 mg H_2O. Found %: C 68.48, 68.22; H 12.10, 12.05. $C_9H_{19}ON$. Calculated %: C 68.74; H 12.18.

Picrate. When alcoholic solutions of the base and of picric acid were mixed together, crystals of the picrate settled out after part of the solvent had been driven off. M.p. 181-182° (from alcohol.)

Picrolonate. When an alcoholic solution of crystalline 1,2,3,6-tetramethyl-4-piperidol was mixed with a hot solution of picrolonic acid and the solution cooled, the crystals of the picrolonate settled out; m.p. 213-214° (from alcohol). After the crystalline 1,2,3,6-tetramethyl-4-piperidol (7 g) had been filtered out, the filtrate was dissolved in a small quantity of alcohol and mixed with a hot solution of 13.6 g of picric acid in 120 ml of alcohol. Fractional crystallization of the resultant picrates yielded 3.5 g of the picrate described above, with a m.p. of 181-182°, from which we secured the crystalline 1,2,3,6-tetramethyl-4-piperidol, with a m.p. of 77-79°. We also secured 8.5 g of a picrate with a m.p. of 104-106° (from alcohol); decomposing this picrate with a 50% aqueous solution of potash, first in the cold and then by heating on a water bath yielded 2.5 g of the liquid isomer of 1,2,3,6-tetramethyl-4-piperidol (VI) with a b. p. of 92-93° at 4 mm; n_D^{20} 1.4830.

4.420 mg substance: 11.080 mg CO_2; 4.830 mg H_2O. 4.108 mg substance: 10.300 mg CO_2; 4.470 mg H_2O. Found %: C 68.41, 68.42; H 12.23, 12.18. $C_9H_{19}ON$. Calculated %: C 68.74; H 12.18.

Picrolonate. When an alcoholic solution of the liquid isomer of 1,2,3,6-tetramethyl-4-piperidol was heated with a solution of picrolonic acid and then allowed to cool, the crystals of the picrolonate settled out; m.p. 202-204° (from alcohol.)

A mixture of the picrates of the isomeric 1,2,3,6-tetramethyl-4-piperidols also yielded about 0.4 g of the dipicrate of 1,2,3,6-tetramethyl-4-methylaminopiperidine with a m.p. of 232-233°, previously described [6] and only slightly soluble in alcohol, which was produced by reducing 1,2,3,6-tetramethyl-4-methylaminopiperidine, which was, in turn, produced by the action of an excess of monomethylamine upon 1,2,3,6-tetramethyl-4-piperidone during the course of the latter's synthesis. The mixed melting point of this dipicrate with the dipicrate of pure 1,2,3,6-tetramethyl-4-methylaminopiperidine exhibited no depression.

2,5-Dimethyl-6-ethyl-4-piperidol (VII). 5 g of 2,5-dimethyl-6-ethyl-4-piperidone (b.p. 80-81° at 7 mm; n_D^{20} 1.4658) was dissolved in 140 ml of absolute alcohol, and 13 g of metallic sodium, in small pieces, was gradually added to the solution. The product was diluted with 50 ml of water and neutralized by adding 60 ml of concentrated hydrochloric acid. The precipitated sodium chloride was filtered out, and the filtrate evaporated to a volume of 35-40 ml in a porcelain dish on a water bath. Sodium hydroxide was added to the aqueous solution, the precipitated base being extracted with ether, dried with fused alkali, and fractionated in vacuo. This yielded 3.8 g of a mixture of the isomeric 2,5-dimethyl-6-ethyl-4-piperidols, with a b.p. of 89-94° at 5 mm; n_D^{23} 1.4770. The product crystallized in part two days later. The crystals were pressed out on a glass filter, washed with acetone, and recrystallized from benzene. Colorless needles with a m.p. of 136-137°.

3.234 mg substance: 8.140 mg CO_2; 3.600 mg H_2O. 5.456 mg substance: 13.769 mg CO_2; 6.125 mg H_2O. Found %: C 68.69, 68.87; H 12.46, 12.56. $C_9H_{19}ON$. Calculated %: C 68.74; H 12.10.

The picrate was prepared by dissolving 0.1 g of the base (m.p. 136-137°) in 5-6 ml of a saturated alcoholic solution of picric acid. One hour later crystals of the picrate began to form. M.p. 226-228° after recrystallization from alcohol (darkens at 215-220°).

2-Methyl-6-ethyl-5-propyl-4-piperidol (VIII). 5.2 g of 2-methyl-6-ethyl-5-propyl-4-piperidone (b.p. 81-82° at 3 mm; n_D^{20} 1.4644) was dissolved in 130 ml of absolute alcohol, and 13 g of metallic sodium was added in small pieces. The product was distilled with 50 ml of water and neutralized by adding 60 ml of concentrated hydrochloric acid. The sodium chloride was filtered out of the solution, which was evaporated in a porcelain dish on a water bath to a volume of 50 ml. The free base was isolated from the aqueous solution by adding a solid alkali and extracting with ether. After the ether had been driven off the residue crystallized partially. When we endeavored to crystallize from benzene and ligroin, we secured a few crystals saturated with oil.

When the reaction product was heated with water to 60-70°, solid crystals settled out; they were collected and pressed out on a porous porcelain plate to remove the traces of oil. A waxy mass was scraped off the plate, which was recrystallized from benzene, yielding 2-methyl-6-ethyl-5-propyl-4-piperidol (VIII), with a m.p. of 123°.

3.351 mg substance: 8.640 mg CO_2; 3.730 mg H_2O. 3.291 mg substance: 8.490 mg CO_2; 3.690 mg H_2O. Found %: C 70.36, 70.40; H 12.45, 12.55. $C_{11}H_{23}ON$. Calculated %: C 70.76; H 12.51.

The picrate was prepared by dissolving 0.1 g of the base (m.p. 123°) in 5 ml of a saturated alcoholic solution of picric acid. One hour later the crystals began to settle out. M.p. 220° after recrystallization from alcohol.

2-Methyl-4-hydroxydecahydroquinoline. 11 g of 2-methyl-4-ketodecahydroquinoline (b.p. 107° at 3 mm; n_D^{20} 1.4990) was dissolved in 400 ml of alcohol and stirred while 30 g of metallic sodium, cut into small bits, was added to the solution. The product was neutralized by adding 140 ml of concentrated hydrochloric acid, the sodium chloride being filtered out of the alcoholic solution and washed on the filter with hot alcohol. The filtrate was evaporated to a volume of 60-70 ml and decomposed by the action of a solid alkali. The separating layer of the base was extracted with ether. When the ether was driven off from the ether solution that had been dried with potash, crystals impregnated with a thick oil settled out. Repeated boiling with ligroin yielded about 7 g of a mixture of crystals, subsequent crystallization of which from acetone yielded the low-melting isomer of 2-methyl-4-hydroxydecahydroquinoline (IX), with a m.p. of 111-113° (from acetone), which was readily soluble in acetone.

4.280 mg substance: 11.119 mg CO_2; 4.374 mg H_2O. 5.368 mg substance: 13.985 mg CO_2; 5.628 mg H_2O. Found %: C 70.90, 71.08; H 11.60, 11.70. $C_{10}H_{19}ON$. Calculated %: C 70.95; H 11.32.

We also secured the high-melting isomer of 2-methyl-4-hydroxydecahydroquinoline (X), with a m.p. of 185-186°, which was less soluble in acetone.

5.720 mg substance: 14.827 mg CO_2; 5.678 mg H_2O. 3.225 mg substance: 8.348 mg CO_2; 3.280 mg H_2O. Found %: C 70.74, 70.64; H 11.10, 11.30. $C_{10}H_{19}ON$. Calculated %: C 70.95; H 11.32.

SUMMARY

Reducing substitution derivatives of the γ-piperidones with metallic sodium in alcohol or catalytically hydrogenating them above a nickel or platinum catalyst yields the corresponding alcohols of the piperidine series, usually as a mixture of two or more stereoisomers. The relative proportions of these isomers may vary widely, depending upon the reaction conditions. In the case of 2,5-dimethyl-4-piperidone, reduction with metallic sodium in alcohol results in the formation of individual 2,5-dimethyl-4-piperidol with a m.p. of 96-97°, whereas catalytic hydrogenation with an Ni catalyst yields a mixture of stereoisomers, the 2,5-dimethyl-4-piperidol with a m.p. of 138° predominating. Reducing the carbonyl group in γ-piperidones that have three or more substituents attached to the piperidine ring yields complex mixtures of stereoisomers of the γ-piperidols.

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Institute of Organic Chemistry,
USSR Academy of Sciences

139. HETEROCYCLIC COMPOUNDS.

XV. Synthesis of Thiopyran Acids by Condensing Tetrahydro-γ-Thiopyrones with Ethyl Cyanacetate and Bromoacetate

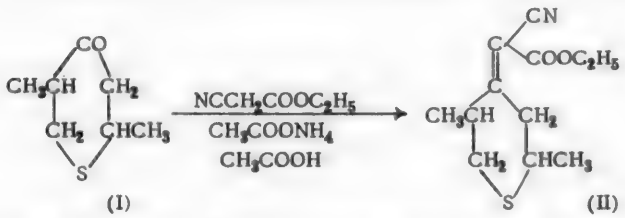
I. N. Nazarov and A. I. Kuznetsova

We recently published a new and simple method of synthesizing various tetrahydro-γ-thiopyrones [1], which can be used as initial products in the search for and synthesis of new physiologically active and medicinal substances.

We know from the literature that the sulfone corresponding to the amide of 4-benzyltetrahydro-1-thiopyran-4-carboxylic acid is an anesthetic [2].

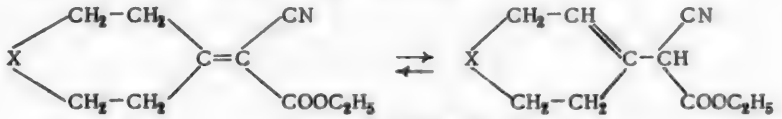
In synthesizing thiopyran acids we investigated the condensation of 2,5-dimethyl-tetrahydro-1-thiopyran-4-one (I) with ethyl cyanacetate and bromoacetate. As in the simple aliphatic ketones [3] and in 1-methyl-4-piperidone [4], we were unable to condense the thiopyrone (I) with malonic ester in the presence of ammonium acetate or piperidine and acetic acid. Nor was this condensation successful when sodium ethylate and sodium iodide were employed, though a yield of 25-30% was secured when cyclohexanone was treated under these same conditions [5].

When we condensed the thiopyrone (I) with ethyl cyanacetate in a benzene solution containing ammonium acetate and acetic acid, continuously removing the water produced from the reaction zone [4], we obtained the ethyl ester of 2,5-dimethyltetrahydro-4-thiopyrylidenecyanacetic acid (II), the yield being 75%:



(I) (II)

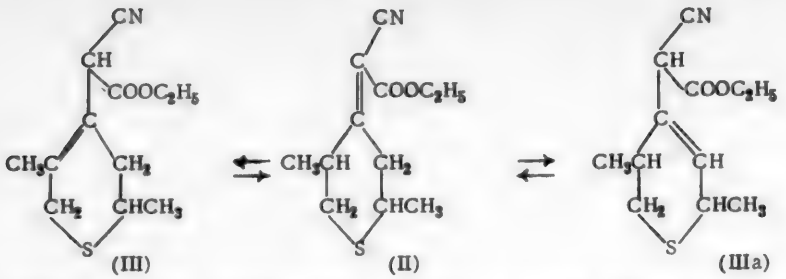
The problem of the structure of cyclohexylidine cyanacetate, which is an analog of the compound (II) we have synthesized, has been discussed in the literature for a long time [6]. The problem of the structure of the condensation products of γ-piperidones and ethyl cyanacetate has been recently resolved. It has been shown that compounds of this sort can react in two tautomeric forms:



X = CH_2, CH_3N

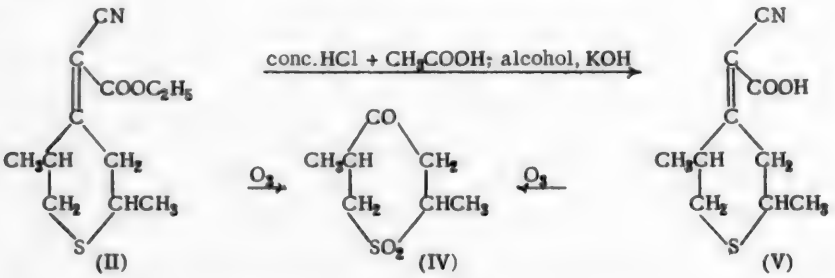
These compounds possess a dual reactivity. On the one hand, they can react like compounds possessing a double bond conjugated with a carbonyl group, while on the other, they enter into reactions that are characteristic of an active hydrogen atom in the ethyl cyanacetate itself.

Apparently, the ethyl thiopyrylidenecyanacetate (II) we have synthesized can likewise react in two tautomeric forms (II-III) or (II-IIIa):



(III) (II) (IIIa)

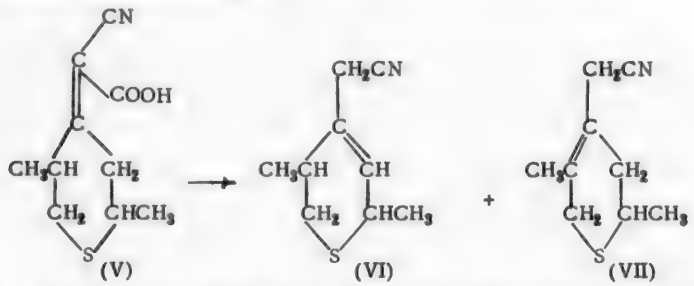
Ozonating the ethyl thiopyrylidenecyanacetate (II) yielded the sulfone (IV) we have described previously [1]. The nitrile group of the compound (II) is highly stable, being saponified neither under alkaline or acid conditions. The principal result of saponifying the ethyl thiopyrylidenecyanacetate (II) with an alcoholic solution of potassium hydroxide is the cleavage of the molecule at the double bond, yielding the thiopyrone (I) and a small quantity of 2,5-dimethyltetrahydro-4-thiopyrylidenecyanacetic acid (V), the m.p. of which is 162-163°. Ethyl thiopyrylidenecyanacetate (II) is unaffected by dilute mineral acids. When it is heated in an acetic acid solution with concentrated sulfuric acid, a high yield of thiopyrylidenecyanacetic acid (V) is produced, ozonation of which yields the cyclic sulfone (IV):



(II) (IV) (V)

The action of methylmagnesium iodide on ethyl thiopyrylidenecyanacetate (II) evolved methane, which is evidence of the presence of a mobile hydrogen atom and, hence, of 21-22% of the tautomeric form (III) or (IIIa).

As several authors have pointed out [7], decarboxylating alkylidenecyanacetic acids proceeds smoothly when these acids are heated to 160-180° in vacuo, and involves the migration of the double bond to the γ-position. Thiopyrylidenecyanacetic acid (V) is also decarboxylated readily under these conditions, the double bond shifting to the ring, yielding a mixture of the nitriles of 2,5-dimethyl-$\Delta^{3,4}$-dihydro-4-thiopyranacetic acid (VI) and 2,5-dimethyl-$\Delta^{4,5}$-dihydro-4-thiopyranacetic acid (VII):

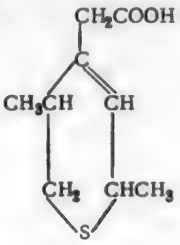


(V) (VI) (VII)

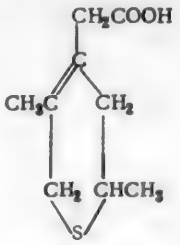
The β,γ-position of the double bond in these compounds is established by the absence of exaltation of the molecular refraction, and by the complete absence of the cyclic sulfone (IV) in the ozonation products of these nitriles.

No ammonia was evolved nor was the thiopyrone (I) formed when a mixture of the nitriles (VI) and (VII) was boiled with an alcoholic solution of potassium hydroxide, so that the nitrile group was not saponified nor did cleavage occur at the double bond thereby. When the nitriles (VI) and (VII) were heated to 70-80° with concentrated hydrochloric acid in acetic acid, we secured a mixture of acid amides, which were not isolated in the pure state and

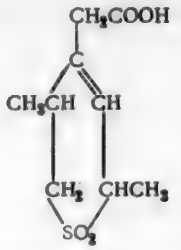
were then saponified by boiling them with a solution of potassium hydroxide in isoamyl alcohol. This yielded a mixture of the respective unsaturaturated acids (VIII) and (IX) as a viscous liquid, from which we isolated a small quantity of the crystals of individual 2,5-dimethyl-$\Delta^{3,4}$-dihydro-4-thiopyranacetic acid (VIII) with an m.p. of 94-95°.



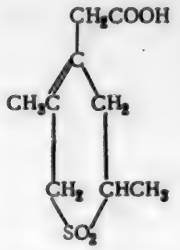
(VIII) m.p. 94-95°



(IX) m.p. 88-89°



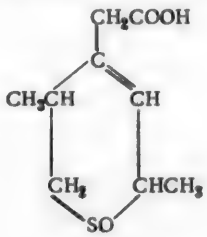
(X) m.p. 185°



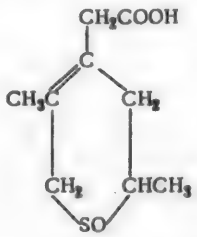
(XI) m.p. 146-147°

Oxidation of the latter with perhydrol in glacial acetic acid yielded the corresponding sulfone (X) with an m.p. of 185°.

We succeeded in separating the liquid mixture of the unsaturated acids (VIII) and (IX) by using the crystalline sulfones (X) and (XI). Oxidation of the liquid mixture of the acids (VIII) and (IX) with perhydrol at room temperature yielded the sulfoxide (XIII), with an m.p. of 255-256°, the second sulfoxide (XII) not being secured in this procedure. Boilding the sulfoxide (XIII) with perhydrol in glacial acetic acid yielded the sulfone (XI) with an m.p. of 146-147°. The residue left after the sulfoxide had been filtered out also yielded the two sulfones (X) and (XI), the m.p. of which were 185° and 146-147°.



(XII)

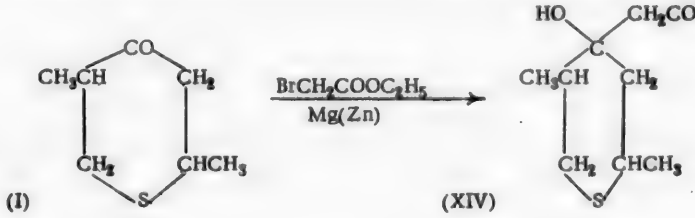


(XIII) m.p. 255-256°

The unsaturated acids (VIII) and (IX) we have synthesized, and their sulfones (X) and (XI), do not add ozone at the double bond, while oxidizing them with permanganate results in far-reaching destruction of the molecule. The oxidation products contain absolutely no sulfone (IV), so that these compounds do not contain a semicyclic double bond. Hence, the only possible explanation for the isomerism of these compounds is the position of the double bond in the ring, even though this position has not been definitely established, because of the difficulty of identifying the oxidation products.

When we consider the transformations described above, beginning with the synthesis of ethyl thiopyrylidenecyanacetate (II) and ending with the formation of the dihydrothiopyranacetic acids (VIII) and (IX), we may regard it as certain that the shift of the double bond from the alpha-beta position to the beta, gamma position took place during the decarboxylation of thiopyrylidenecyanacetic acid (V). There are references in the literature to the feasibility of the migration of the double bond in alpha, beta unsaturated acids when acted upon by acids or bases [8].

The second part of our research involved the condensation of the thiopyrone (I) by the Reformatsky method [9] with ethyl bromoacetate and magnesium [10]. This condensation yielded a mixture of geometric isomers of the ester of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XIV), the yield being 53%:



(I) (XIV)

b) Ozonized oxygen (5% ozone) was passed through a solution of 0.15 g of the acid (m.p. 94-95°) in 30 ml of chloroform for one hour at the rate of 5 liters per hour. After 20 ml of water had been added, the mixture was heated for 2 hours. The solution was evaporated to dryness, yielding 0.1 g of crystals of the sulfone (X), which had an m.p. of 185° and exhibited no depression with the preceding sample.

When ozonized oxygen (6% ozone) was passed through a chloroform solution of the sulfone (m.p. 185°) for 10 hours, no ozone was added at the double bond, the recovered sulfone having the same m.p. of 185° and exhibiting no depression with the initial sample. Similarly, the ozone was not added at the double bond of the isomeric sulfone (XI), with an m.p. of 146-147°.

Oxidizing a mixture of the 2,5-dimethyldihydro-4-thiopyranacetic acids (VIII) and (IX). 4.5 g of the mixture of the unsaturated acids(VIII) and (IX) described above, produced by saponifying the nitriles (VI) and (VII), was dissolved in 565 ml of glacial acetic acid, and 6.75 ml of 30% perhydrol was added to the solution. Two hours later the acetic acid was driven off in vacuo, the bath temperature not exceeding 50°. The thick residue was diluted with ether, precipitating 1.4 g of crystals of the sulfoxide (XIII), whose m.p. was 255-256° after repeated recrystallization from alcohol.

2.682 mg substance: 5.188 mg CO_2; 1.692 mg H_2O; 1.300 mg SO_4. 1.900 mg substance: 3.675 mg CO_2. 1.208 mg H_2O; 0.930 mg SO_4. Found %: C 52.79; H 7.06, 7.11; S 16.18, 16.34. $C_9H_{14}O_3S$. Calculated %: C 53.44, H 6.98; S 15.85.

After the sulfoxide had been filtered out of the ether solution, the ether was driven off, leaving a residue of 3.4 g of a hyaline substance. When this residue was diluted with water and rubbed with a rod, crystals of the sulfone (X) with an m.p. of 185°, described above, settled out. The aqueous solution was evaporated and rediluted with water; rubbing with a rod again threw down the sulfone with an m.p. of 185°. This operation was repeated one more time. This yielded a total of 0.5 g of the sulfone with an m.p. of 185°, which exhibited no depression when mixed with the sample described above. The remaining acid was diluted with ether, after which rubbing with a rod threw down the crystals of the other sulfone (XI), with an m.p. of 146-147°, which was also produced by oxidizing the sulfoxide described above.

0.2 gram of the sulfoxide (XII) (m.p. 255-256°) dissolved in 5 ml of glacial acetic acid, was boiled for 4 hours with 0.15 ml of 30% perhydrol. The reaction product was diluted with water (2 ml) and evaporated to dryness. This yielded 0.2 g of the other isomer of the sulfone (XI), with an m.p. of 146-147° (from water).

5.580 mg substance: 10.072 mg CO_2; 3.320 mg H_2O; 2.465 mg SO_4. 5.617 mg substance: 10.160 mg CO_2; 3.237 mg H_2O; 2.420 mg SO_4. Found %: C 49.26, 49.36; H 6.66, 6.45; S 14.74, 14.36. $C_9H_{14}O_4S$. Calculated %: C 49.52; H 6.46; S 14.69.

Oxidizing the sulfones (X) and (XI) with permanganate. Since neither of the isomeric sulfones (X) and (XI) adds ozone at the double bond, they were both oxidized with permanganate.

a) 0.6 grams of permanganate was gradually added, with stirring, to a solution of 0.5 g of the sulfone (m.p. 185°) in 40 ml of acetone and 1.5 ml of 10% sulfuric acid. Oxidation was carried out at room temperature and was finished in 30 minutes. The solution was completely decolorized. The customary treatment recovered 0.2 g of the sulfone with an m.p. of 185°. (Its mixed melting point with the initial product exhibited no depression.) Moreover, we obtained a small quantity of liquid acid products.

b) 50 ml of a 2% aqueous permanganate solution was gradually added, with stirring to a solution of 0.8 g of the sulfone (XI) (m.p. 146-147°) in 50 ml of acetone and 2.2 ml of 10% sulfuric acid. After the solution had been completely decolorized, the product was processed in the usual manner. This recovered 0.2 g of the sulfone with an m.p. of 146-147° (its mixed melting point exhiting no depression) plus traces of acid products.

Ethyl ester of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XIV): 36 grams of 2,5-dimethyltetrahydro-1-thiopyran-4-one (I) and 42 g of ethyl bromoacetate were dissolved in 150 ml of absolute benzene. 25 ml of the solution and 6 g of magnesium were placed in a three-necked flask, fitted with a mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer. A crystal of iodine was added, and the solution was heated on a water bath. A vigorous reaction set in at 65°. The bath was removed, the process being controlled by gradually adding the rest of the solution. The reaction mass was refluxed for 4.5 hours on a water bath and left to stand overnight. The next day the flask was chilled with ice water as the product was

hydrolyzed with 15% acetic acid (240 ml), extracted with ether, washed with a bicarbonate solution, and dried with magnesium sulfate. Fractionation in vacuo recovered 7.1 g of the unreacted thiopyrone (I) and yielded 23.0 g of the ethyl ester of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XIV) as a colorless liquid:

B.p./4 mm 134°; n_D^{20} 1.4941; d_4^{20} 1.0966; MR 61.69; calculated 61.95.
4.073 mg substance: 1.752 ml 0.02 N I_2. Found %: S 13.79. $C_{11}H_{20}O_2S$. Calculated %: S 13.79.

Oxidizing the thiopyranol (XIV) to a sulfone. 20 ml of a 4% aqueous solution of permanganate was added, with ice-water chilling to a solution of 1 g of the thiopyranol (XIV) in 10 ml of acetone and 3.8 ml of 10% sulfuric acid. The manganese dioxide was washed with hot water, and the product was thoroughly extracted with ether, dried with magnesium sulfate and distilled in vacuo. This yielded 0.5 g of the sulfone as a noncrystallizing hyaline mass, with a b.p. of 183-185° at 0.5 mm; n_D^{20} 1.4931.

3.635 mg substance: 6.770 mg CO_2; 2.550 mg H_2O; 1.390 mg SO_4. 4.620 mg substance: 8.585 mg CO_2; 3.155 mg H_2O; 1.780 mg SO_4. Found %: C 50.85, 50.71; H 7.49, 7.64; S 12.75, 12.86. $C_{11}H_{20}O_3S$. Calculated %: C 49.97; H 7.62; S 12.13.

Amide of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XV). 6 ml of a 30% aqueous solution of ammonia was added to 2 g of the ester (XIV). The liquid, which had become homogeneous after one month had elapsed, was extracted with ether. The ether solution was dried and the ether driven off, the residue yielding 1.2 g of a thick, syrupy liquid, which crystallized when rubbed with a rod. The crystals were filtered out and recrystallized from benzene. This yielded 0.2 g of the amide (XV), which had an m.p. of 123-124°.

3.403 mg substance: 0.824 ml 0.02 N $KH(IO_3)_2$. 3.019 mg substance: 0.745 ml 0.02 N $KH(IO_3)_2$. 4.310 mg substance: 8.400 mg CO_2; 3.327 mg H_2O; 2.020 mg SO_4. 3.960 mg substance: 7.740 mg CO_2. 3.028 mg H_2O. 1.850 mg SO_4. Found %: N 6.78, 6.91; C 53.19, 53.34; H 8.64, 8.55; S 15.65, 15.60. $C_9H_{17}O_2NS$. Calculated %: N 6.89; C 53.16; H 8.43; S 15.77.

The customary processing of the aqueous solution yielded 0.5 g of acid products that were not analyzed.

Saponifying the ethyl ester of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XIV). 1) 5 grams of the ester (XIV) was dissolved in 14 ml of a 10% alcoholic solution of potassium hydroxide. 48 hours later the alcohol was driven off in vacuo, and the residue was dissolved in water and extracted with ether to eliminate the neutral products. The aqueous solution was acidulated with 6 ml of 15% hydrochloric acid and extracted with ether. Drying the product and driving off the ether yielded a residue of 4 g of a mixture of the stereoisomeric hydroxy acids (XVI) as a viscous liquid, which crystallized in part by the next day. The crystals were filtered out and recrystallized repeatedly from benzene. This yielded about 1 g of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XVI) as colorless needles with an m.p. of 132.5-133.5°.

0.1238 g substance: 6.04 ml 0.1 N KOH. 5.835 mg substance: 11.390 mg CO_2; 4.190 mg H_2O; 2.775 mg SO_4. 4.315 mg substance: 8.410 mg CO_2; 3.110 mg H_2O; 2.045 mg SO_4. Found: M 204.08; %: C 53.27, 53.19; H 8.03, 8.06; S 15.88, 15.82. $C_9H_{16}O_3S$. Calculated: M 204.28; %: C 52.90; H 7.89; S 15.69.

After the solid acid had been filtered out, the mother liquor was distilled in vacuo. This yielded about 3 g of a mixture of the stereoisomeric acids (XIV) as a hyaline mass with a b.p. of 150-162° at 0.02 mm.

0.2488 g substance: 12.46 ml 0.1 N KOH. 6.740 mg substance: 13.100 mg CO_2; 4.800 mg H_2O. 5.150 mg substance: 10.020 mg CO_2; 3.660 mg H_2O; 2.410 mg SO_4. Found: M 204.31; %: C 53.04, 53.10; H 7.97, 7.95; S 15.62. $C_9H_{16}O_3S$. Calculated: M 204.28; %: C 52.90; H 7.89; S 15.69.

When these acids were diluted with petroleum ether, crystals settled out, their m.p. being 96-97° after the first recrystallization from benzene, the m.p. rising to 98-99°, 98-102°, and 125-133° after subsequent recrystallizations.

An attempt to separate the isomers of the hydroxy acids (XVI) by recrystallization from other solvents (chloroform, ether, and acetone) was also unsuccessful. Nor could we separate the isomers by means of chromatography.

Oxidizing 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid to a sulfone. An alcoholic solution of 0.2251 g of the hydroxy acid (XVI) (m.p. 132-133°) was back-titrated with a 0.1N solution of potassium hydroxide.

The solution was evaporated, and the residue was dissolved in water and oxidized with 5 ml of a 4% aqueous solution of permanganate. The manganese dioxide was washed with hot water, and the aqueous solution evaporated and acidulated with 30% sulfuric acid. This yielded 0.2 g of the sulfone (XVII), which had an m.p. of 192-193° after recrystallization from water.

8.84 mg substance: 14.98 mg CO_2; 5.52 mg H_2O. 9.09 mg substance: 15.42 mg CO_2; 5.69 mg H_2O. Found %: C 46.24, 46.29; H 6.69, 7.00. $C_9H_{16}O_3S$. Calculated %: C 45.75; H 6.83.

Anilide of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XVIII). 1.15 grams of the hydroxy acid (XVI) (m.p. 132-133°) was heated to 180° for 10 hours with 2 g of freshly distilled aniline. The product was diluted with water, extracted with ether, washed with a 10% solution of hydrochloric acid, and dried with magnesium sulfate. Driving off the ether yielded 0.85 g of the anilide (XVIII), which had an m.p. of 136-137° (from benzene).

5.670 mg substance: 0.264 ml N_2 (20°, 735 mm). 5.608 mg substance: 0.261 ml N_2 (21°, 735 mm). 5.210 mg substance: 12.318 mg CO_2; 3.562 mg H_2O; 1.830 mg SO_4. 5.798 mg substance: 13.700 mg CO_2; 3.920 mg H_2O; 1.980 mg SO_4. Found %: N 5.25, 5.23; C 64.52, 64.48; H 7.65, 7.56; S 11.72, 11.40. $C_{15}H_{21}O_2NS$. Calculated %: N 5.01; C 64.48; H 7.58; S 11.47.

Dehydrating the ethyl ester of 2,5-dimethyltetrahydro-4-thiopyranol-4-acetic acid (XIV). a) 11 g of the hydroxy ester (XIV) was dehydrated by heating it to 150-160° for 3.5 hours with 20 g of finely pulverized anhydrous potassium bisulfate. After the reaction mass had cooled, it was dissolved in water, the product being extracted with ether, dried with magnesium sulfate, and fractionated in vacuo.

Fraction 1: 132-137° at 7 mm; n_D^{22} 1.5010 – 1.05 g;
Fraction 2: 137-142° at 7 mm; n_D^{22} 1.5020 – 1.1 g;
Fraction 3: 142-145° at 7 mm; n_D^{22} 1.5018 – 3 g.

When we saponified Fraction 3 with a 10% alcoholic solution of potassium hydroxide, we got 2.4 g of acids, part of which crystallized. The crystals were filtered out and recrystallized from benzene. This yielded 0.3 g of the second isomer of 2,5-dimethyltetrahydro-4-thiopyranol-acetic acid (XVI), with an m.p. of 116-117°.

0.1327 g substance: 6.52 ml 0.1 N KOH. 4.570 mg substance: 8.900 mg CO_2; 3.368 mg H_2O; 2.120 mg SO_4. Found: M 203.46; %: C 53.15; H 8.24; S 15.49. $C_9H_{16}O_3S$. Calculated: M 204.28; %: C 52.90; H 7.89; S 15.69.

0.1327 gram of this isomer of the hydroxy acid (XVI) (m.p. 116-117°) was dissolved in alcohol and back-titrated with a 0.1N solution of potassium hydroxide. The solution was evaporated to dryness, and the salt of the acid dissolved in 10 ml of water and oxidized with 25 ml of a 5% aqueous solution of permanganate. The customary processing yielded 0.1 g of the second isomer of the sulfone (XVII), with an m.p. of 178-179° (from water).

4.985 mg substance: 8.375 mg CO_2; 3.040 mg H_2O. Found %: C 45.85; H 6.82. $C_9H_{16}O_3S$. Calculated %: C 45.75; H 6.83.

b) 25 grams of the hydroxy ester (XIV) and 25 g of potassium bisulfate were heated to 195-200° for 1.5 hours in a 25-30 mm vacuum. The reaction product was distilled at 110-156°, together with the water. The residue was dissolved in water and extracted with ether, together with the distillate. The product was washed with water, dried with magnesium sulfate, and fractionated in vacuo. This yielded 17 g of a mixture of the unsaturated esters (XIX) and (XX) with a b.p. of 117-124° at 4 mm; n_D^{20} 1.5060.

A narrow fraction in the form of a slightly yellowish liquid was isolated from this mixture for analysis:

B.p./3.5 mm 115-116°; n_D^{20} 1.5063; d_4^{20} 1.0619; MR 59.99; calculated 59.95.

6.540 mg substance: 14.750 mg CO_2; 5.000 mg H_2O; 2.890 mg SO_4. 4.640 mg substance: 10.440 mg CO_2; 3.540 mg H_2O; 2.013 mg SO_4. Found %: C 61.55, 61.40; H 8.55, 8.53; S 14.75, 14.48. $C_{11}H_{18}O_2S$. Calculated %: C 61.64; H 8.47; S 14.96.

After the unsaturated esters (XIX) and (XX) had been driven off, the 0.5 g of residue crystallized in part upon standing. This residue yielded about 0.1 g of 2,5-dimethyl-$\Delta^{4,5}$-dihydro-4-thiopyranacetic acid (IX) as colorless scales, with an m.p. of 88-89° (from water).

6.052 mg substance: 12.905 mg CO_2; 4.100 mg H_2O; 3.155 mg SO_4. 5.805 mg substance: 12.376 mg CO_2; 3.971 mg H_2O; 2.968 mg SO_4. Found %: C 58.19, 58.18; H 7.58, 7.65; S 17.40, 17.07. $C_9H_{14}O_2S$. Calculated %: C 58.03; H 7.57; S 17.21.

0.1 gram of this acid (m.p. 88-89°) was dissolved in 13 ml of glacial acetic acid, and 0.15 ml of 30% perhydrol was added to the solution. Three days later the solution was diluted with water, the water and the acetic acid driven off in vacuo, and the product extracted with ether. This yielded about 0.1 g of the sulfone (XI), which had an m.p. of 146-147° after recrystallization from water and exhibited no depression of the mixed melting point with the sample described above.

Saponifying the unsaturated esters (XIX) and (XX). 15.15 grams of a mixture of the unsaturated esters (b.p. of 117-124° at 4mm) was dissolved in 41 ml of 10% alcoholic potassium hydroxide. A half an hour later the alcohol was driven off in vacuo, the residue being dissolved in 30 ml of water and extracted with ether. Drying and distillation of the ether solution yielded 4.6 g of the unreacted ester (b.p. 117-122° at 4 mm; n_D^{20} 1.5105). Evaporation, acidulation, and ether extraction of the aqueous salt solution yielded 8.5 g of a mixture of the unsaturated acids (IX) and (XXII) with a b.p. of 150-153° at 4 mm; n_D^{20} 1.5335. The following fraction was collected from this mixture for analysis:

B.p./3 mm 146-147°; n_D^{20} 1.5325; d_4^{20} 1.1374; MR 50.78; calculated 50.60:

0.1683 g substance: 8.70 ml 0.1 N KOH.
4.992 mg substance: 3.493 mg H_2O; 10.541 mg CO_2; 2.558 mg SO_4. 4.856 mg substance: 3.392 mg H_2O. 10.271 mg CO_2; 2.462 mg SO_4. Found: M 193.54; %: C 57.62, 57.72; H 7.83, 7.81; S 17.10, 16.93. $C_9H_{14}O_2S$. Calculated: M 186.26; %: C 58.03; H 7.57; S 17.21.

The unreacted unsaturated ester (4.6 g) was resaponified with 14 ml of a 10% alcoholic solution of potassium hydroxide. The customary processing yielded 2 g of 2,5-dimethyltetrahydro-4-thiopyrylideneacetic acid (XXII) as colorless needles with an m.p. of 111-112° (from petroleum ether).

4.645 mg substance: 9.923 mg CO_2; 3.248 mg H_2O; 2.380 mg SO_4. 5.141 mg substance: 10.944 mg CO_2; 3.560 mg H_2O; 2.640 mg SO_4. Found %: C 58.30, 58.10; H 7.82, 7.75; S 17.10, 17.14. $C_9H_{14}O_2S$. Calculated %: C 58.03; H 7.57; S 17.21.

Oxidizing 2,5-dimethyltetrahydro-4-thiopyrylideneacetic acid to a sulfone (XXIII). a) 0.2 gram of the unsaturated acid (XXII) (m.p. 111-112°) was dissolved in 26 ml of glacial acetic acid, and 0.3 ml of 30% perhydrol was added to the solution. Two days later the acetic acid was driven off in vacuo, the residue being diluted with water and extracted with ether. The resultant sulfone (XXIII) had an m.p. of 197-198° (from water).

3.948 mg substance: 7.118 mg CO_2: 2.355 mg H_2O; 1.730 mg SO_4. 5.123 mg substance: 9.207 mg CO_2: 3.079 mg H_2O; 2.241 mg SO_4. Found %: C 49.20, 49.05; H 6.67, 6.72; S 14.62, 14.61. $C_9H_{14}O_4S$. Calculated %: C 49.52; H 6.46; S 14.69.

b) 1 gram of the mixture of the unsaturated acids (IX) and (XXII) (b.p. 153-160° at 4 mm) described above was dissolved in 130 ml of glacial acetic acid, and 1.5 ml of 30% perhydrol was added to the solution. Four days later the acetic acid was driven off in vacuo, and the reaction product was allowed to stand 8 days in an open container. The resultant oily liquid was washed with ether and dissolved in alcohol, the crystals that settled out the following day being filtered out and recrystallized from water. The resultant sulfone (XXIII) had an m.p. of 197-198° and exhibited no depression when mixed with the previous sample.

Anilide of 2,5-dimethyltetrahydro-4-thiopyrylideneacetic acid(XXIV). a) 0.5 gram of the unsaturated acid (XXII) (m.p. 111-112°) and 1.5 g of aniline were refluxed together for 10 hours. The anilide of 2,5-dimethyltetrahydro-4-thiopyrylideneacetic acid(XXIV) produced by the customary processing had an m.p. of 154° (from alcohol).

6.320 mg substance: 0.316 ml N_2 (25°, 744 mm). 6.638 mg substance: 0.327 ml N_2 (25°, 744 mm). Found %: N 5.61, 5.56. $C_{15}H_{19}ONS$. Calculated %: N 5.28.

b) 1.5 g of the mixture of the unsaturated acids (IX) and (XXII) (b.p. 153-160° at 4 mm) and 6 g of aniline were refluxed together for 13 hours. The customary processing yielded 0.8 g of the anilide (XIV) with an m.p. of 153-154°, which exhibited no depression when mixed with the preceding sample.

Ozonating 2,5-dimethyltetrahydro-4-thiopyrylideneacetic acid. Ozonized oxygen (6% ozone) was passed through a solution of 0.4 g of the acid (XXII) (m.p. 111-112°) in 50 ml of chloroform for 1.5 hours at the rate of 5 liters per hour. The oxonide was hydrolyzed by heating it in water (6 hours at 60°), the customary treatment of the neutral products yielding 0.15 g of the sulfone (IV), whose m.p. was 138° after recrystallization from alcohol, exhibiting no depression when mixed with a known sample.

Dehydrating the hydroxy acids (XIV). 3.5 grams of the steroisomeric hydroxy acids (XVI), produced by saponifying the esters (XIV), was heated to 200-220° for 1.5 hours in a 15-mm vacuum together with 3.5 g of potassium bisulfate. The customary processing yielded 1.3 g of the unsaturated acids (IX) and (XXII) described above, with a b.p. of 148-154° at 4 mm; n_D^{20} 1.5305. These acids (1.3 g) were boiled for 12 hours with 2 g of aniline. This yielded 0.4 g of the anilide of 2,5-dimethyltetrahydro-4-thiopyrylideneacetic acid (XXIV), which had an m.p. of 154° and exhibited no depression when mixed with the sample described above.

SUMMARY

Condensation of 2,5-dimethyltetrahydro-1-thiopyran-4-one (I) with ethyl cyanacetate and bromoacetate produced high yields of the thiopyran esters (II) and (XIV). Saponifying the ethyl thiopyrylidenecyanacetate (II) yielded the acid (V), which was decarboxylated by heat (to 170-180°), while the double bond was shifted to the ring and a mixture of the isomeric nitriles (VI) and (VII) was produced. Saponifying these nitriles yielded the dihydrothiopyranacetic acids (VIII) and (IX), which were oxidized to the corresponding crystalline sulfones (X) and (XI).

When the hydroxy ester (XIV) was saponified, we obtained two stereoisomeric hydroxy acids (XVI), the thiopyrylideneacetic acid (XXII), together with a trace of the acid (IX), being the principal product of their dehydration. When the hydroxy acid (XIV) was dehydrated, the principal product again was an unsaturated ester (XIX) with a semicyclic double bond, saponification of which yielded the acid (XXII) with a small percentage of the unsaturated ester (XX), with a double bond in the ring. The unsaturated esters (II), (XIX), and (XX), the acids (VIII), (IX), and (XXII), and the sulfones (X), (XI) and (XXIII) are not hydrogenated in alcohol, dioxane, and acetic acid solutions by Pt and Pd catalysts, even at 100°.

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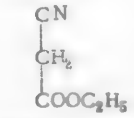
Institute of Organic Chemistry,
U.S.S.R. Academy of Sciences

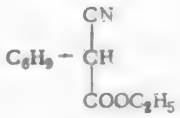
RESEARCH ON SUBSTITUTION DERIVATIVES OF ETHYL CYANACETATE AND OF THE PRODUCTS OF THEIR INTERACTION WITH ACETYLMETHYLUREA

N. V. Khromov-Borisov and I. M. Yurist

The ethyl esters of cyanacetic (I) cyclohexenylcyanacetic (II) and methylcyclohexenylcyanacetic (III) acids are intermediate products in the synthesis of the sodium salt of 5-cyclohexenyl-3,5-dimethylbarbituric acid or hexenal (IV).



(I)



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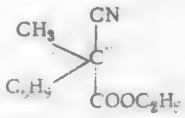

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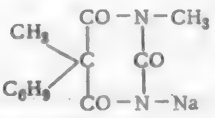
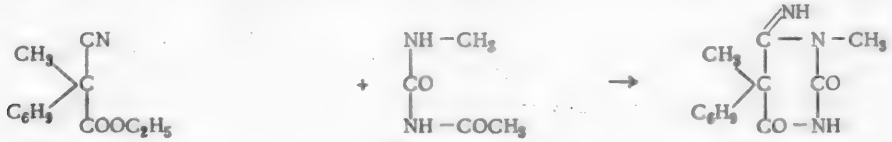


(IV)

In industrial production the ethyl methylcyclohexenylcyanacetate (III) produced by methylating ethyl cyclohexenylcyanacetate (II) usually contains the initial unmethylated ester as an impurity, since these esters have adjacent boiling points and thus are hard to separate by fractionation. As a result the methylcyclohexenylcyanacetic ester used in the condensation with acetylmethylureau (V) usually contains 10-12% of the cyclohexenylcyanacetic ester.

When reacted with acetylmethylurea, the former (III) yields 5-cyclohexenyl-4-imino-3,5-dimethylbarbituric acid (VI):

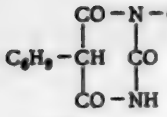


(III) (V) (VI)

which are dissolved in the cold (0-5°) in dilute hydrochloric acid, the hydrochloric acid solution being converted by heat into 5-cyclohexenyl-3,5-dimethylbarbituric acid (VII), which is precipitated out:

(VI) (VII)

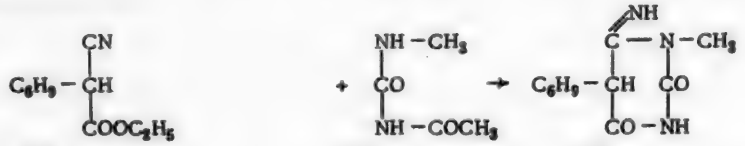
When the unmethylated ester (II) is reacted with acetylmethylurea (V), we get a solid that is insoluble in dilute mineral acids, is not saponified by heating with acids, and constitutes a waste product. The hypothesis advanced by some researchers that this substance is 5-cyclohexenyl-3-methylbarbituric acid (VIII) seemed to us to be unlikely for the following reasons. It has been established [1, 2] that the condensation of cyanacetates



(VIII)

and their derivatives with methylurea and its derivatives yields 3-methyl-4-imino-barbituric acids, which can be converted into the corresponding barbituric acids only by subsequent saponification in an acid medium. It was hard to suppose that 3-methyl-4-imino-5-cyclohexenylbarbituric acid (IX) can be saponified by hydrochloric acid without the use of heat. Thus the structure of this compound remained indeterminate.

This product was collected, purified, and indentified to establish its structure. The product had an m.p. of 195-196° after repeated recrystallizations from alcohol. The elementary analysis indicated that its composition of ($C_{11}H_{13}O_2N_3$) corresponded to 3-methyl-4-imino-5-cyclohexenylbarbituric acid. We synthesized this acid by condensing the cyclohexenylcyanacetic ester (II) with acetylmethylurea (V). The synthesized product's m.p. was 195-196° after crystallization from alcohol, while its elementary composition corresponded to the same formula of $C_{11}H_{13}O_2N_3$. The mixed melting point of the two substances indicated no depression. Hence, the condensation by-product was identified as 3-methyl-4-imino-5-cyclohexenylbarbituric acid (IX), produced by the condensation of the cyclohexenylcyanacetic ester (II), contained in the methylcyclohexenylcyanacetic ester (III), with acetylmethylurea (V):

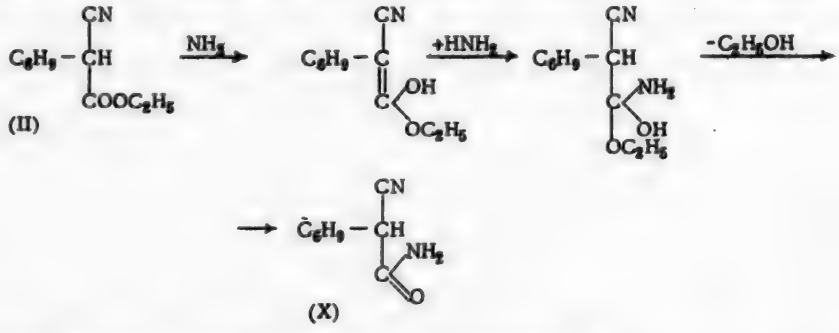


(II) (V) (IX)

The sodium salt of 3-methyl-4-imino-5-cyclohexenylbarbituric acid proved to be more toxic than hexenel when tested on rabbits and possessed no soporific action.

The question then arose of developing a method for freeing the methylcyclohexenylcyanacetic ester from the cyclohexenylcyanacetic ester it contained. We know [1, 3, 4, 5] that unsubstituted and monosubstituted malonic, acetoacetic, and cyanacetic esters form acid amides with ammonia, while the corresponding disubstituted esters do not react with ammonia. Our experiments have shown that the action of aqueous ammonia upon a mixture of the cyclohexenylcyanacetic and methylcyclohexenylcyanacetic esters converts the former into the amide (X) while the latter remains unaffected.

The following diagram may explain the interaction of the cyclohexenylcyanacetic ester with ammonia:



(II) (X)

This diagram explains why such a reaction is impossible with disubstituted esters.

After the precipitated amide and the aqueous ammonia layer had been removed, the ester was dried with calcium chloride and distilled in vacuo. The ester thus purified produced no 3-methyl-4-imino-5-cyclohexenylbarbituric acid when condensed with acetylmethylurea.

We also employed this reaction with ammonia to make a quantitative determination of the cyanacetic and cyclohexenylcyanacetic esters in the presence of methylcyclohexenylcyanacetic ester. The accuracy of the analysis method we have elaborated is $\pm 0.5\%$.

It should be pointed out at this juncture that when pure (95-96%) cyclohexenylcyanacetic ester and a fraction that contains only 10-12% of this ester are treated with concentrated aqueous ammonia, we get compounds whose composition is the same, but whose melting points differ (192-193° with decomposition and 115-116°, respectively). The titration data indicate that both compounds are produced by the reaction of 1 mole of the cyclohexenylcyanacetic ester with 1 mole of ammonia. Their elementary analysis shows that both compounds are amides of cyclohexenylcyanacetic acid. It may be that the resultant amide is condensed when the pure cyclohexenylcyanacetic ester is reacted with ammonia, whereas the reaction of ammonia with the

the cyclohexenylcyanacetic ester with 1 mole of ammonia. Their elementary analysis shows that both compounds are amides of cyclohexenylcyanacetic acid. It may be that the resultant amide is condensed when the pure cyclohexenylcyanacetic ester is reacted with ammonia, whereas the reaction of ammonia with the cyclohexenylcyanacetic ester dissolved in ten times its weight of methylcyclohexenylcyanacetic ester involves no condensation.

EXPERIMENTAL

1. Synthesis of 3-methyl-4-imino-5-cyclohexenylbarbituric acid (IX). 19.3 grams of cyclohexenylcyanacetic ester and 11.6 g of acetylmethylurea were added to a solution of 2.3 g of metallic sodium in 25 ml of absolute methanol. Condensation was effected at 65° for 6 hours in a closed vessel fitted with a reflux condenser. The solvent was driven off in vacuo (30-50 mm), the temperature of the mass being 50-60°. The residue was dissolved with cold water (60 ml), and the oily by-product of the reaction was separated. The aqueous layer was chilled to 0° and neutralized with chemically pure hydrochloric acid until its reaction was neutral. The precipitate was suction-filtered, washed with water, and crystallized twice from 50% alcohol. M.p. 195-196°.

The elementary composition confirmed that 3-methyl-4-imino-5-cyclohexenylbarbituric acid had been formed.

4.564 mg substance: 10.111 mg CO_2; 2.870 mg H_2O. 4.478 mg substance: 9.900 mg CO_2; 2.804 mg H_2O. 2.522 mg substance: 0.426 ml N_2 (19°, 743 mm). 1.746 mg substance: 0.297 ml N_2 (20.5°, 740 mm). Found %: C 60.42, 60.29; H 7.04, 7.01; N 19.31, 19.33. $C_{11}H_{13}O_2N_3$. Calculated %: C 59.73; H 6.79; N 19.00.

3-Methyl-4-imino-5-cyclohexenylbarbituric acid is soluble in hot water and when heated in dilute hydrochloric and sulfuric acids, settling out unchanged when the solutions cool. It is soluble in the cold in dilute alkali solutions (both aqueous and alcoholic), settling out again when the solutions are acidulated. When an alkaline solution is heated, the characteristic odor of cyclohexanone is perceptible.

Attempts to methylate 3-methyl-4-imino-5-cyclohexenylbarbituric acid with methyl iodide in the presence of sodium ethylate yielded the original product unchanged, m.p. 195-196°. Heating the 3-methyl-4-imino-5-cyclohexenylbarbituric acid to 150° in a sealed tube with 10% hydrochloric acid yielded a reaction product that fused over a wide range (144-155°) after recrystallization from alcohol and contained anywhere from 14 to 17% of nitrogen, depending upon the run. These findings indicate that 3-methyl-4-imino-5-cyclohexenylbarbituric acid is saponified with difficulty even under pressure; in our tests we obtained various mixtures of the initial iminobarbituric acid and its saponification product.

The reaction of the 3-methyl-4-imino-5-cyclohexenylbarbituric acid with sodium nitrite in glacial acetic acid likewise yielded the initial product unchanged.

2. Synthesis of the sodium salt of 3-methyl-4-imino-5-cyclohexenylbarbituric acid. A solution of 0.18 g of chemically pure sodium hydroxide in 40 ml of absolute methanol was added to 1 g of the iminobarbituric acid until its reaction was slightly alkaline (test with thymolpthalein paper). The alcohol was driven off in vacuo to dryness. The dry residue (1.15 g) was a white amorphous powder that was readily soluble in water. Acidulating the solution threw down the original iminobarbituric acid (m.p. 195°). Comparison of the 3-methyl-4-imino-5-cyclohexenylbarbituric acid with the by-product obtained in the synthesis of hexenal indicated the two substances were identical. The by-product had an m.p. of 195-196° after recrystallization from 50% alcohol; its mixed melting point with 3-methyl-4-imino-5-cyclohexenylbarbituric acid exhibited no depression.

0.1523 g substance: 0.3352 g CO_2; 0.0972 g H_2O. 0.3214 g substance: 44.0 ml 0.1 N H_2SO_4. 0.1820 g substance: 25.0 ml 0.1 N H_2SO_4. Found %: C 60.01; H 7.09; N 19.17, 19.23. $C_{11}H_{15}O_2N_3$. Calculated %: C 59.73; H 6.79; N 19.00.

3. Preparation of the pure methylcyclohexenylcyanacetic ester (III). The methylated ester fraction (b.p. 140-147° at 15 mm) was treated with an equal weight of concentrated ammonia at room temperature for 6-7 hours in a vessel fitted with a stirrer. The precipitate was suction-filtered, and the oily layer separated, dried with calcium chloride, and fractionated in vacuo. A 136-138° fraction at 14-15 mm was collected. The specific gravity of the methylcyclohexenylcyanacetic ester produced was d_{20}^{20} 1.036. The yield was 80% of the

processed fraction. The methylcyclohexenylcyanacetic ester thus produced no longer reacted with ammonia; condensing it with acetylmethylurea yielded 3,5-dimethyl-4-imino-5-cyclohexenylbarbituric acid that contained no 3-methyl-4-imino-5-cyclohexenyl-barbituric acid as an impurity.

4. Identification of the amide of cyclohexenylcyanacetic acid (X). a) The solid filtered out during the refining of the ester mixture with ammonia was collected, washed with water, and recrystallized repeatedly from alcohol, and finally from a mixture of alcohol and chloroform. M.p. 115-116°.

0.1648 g substance: 0.3898 g CO_2; 0.1018 g H_2O. 0.1512 g substance: 18.20 ml 0, 1 N H_2SO_4.
Found %: C 65.1; H 6.79; N 16.9. $C_9H_{12}ON_2$. Calculated %: C 65.86; H 7.32; N 17.07.

b) 10 grams of the cyclohexenylcyanacetic ester was processed with 10 g of 25% aqueous ammonia for 6-7 hours in a flask fitted with a stirrer. The mixture was diluted with water (25 ml), the precipitate filtered out, and crystallized repeatedly, first from 70% alcohol and then from a 1:1 mixture of alcohol and chloroform. The m.p. of the resulting white, crystalline substance was 192-193° with decomposition.

0.3020 g substance: 0.7230 g CO_2; 0.2026 g H_2O. 0.2138 g substance: 26.40 ml 0.1 N H_2SO_4.
Found %: C 65.2; H 7.45; N 17.29. $C_9H_{12}ON_2$. Calculated %: C 65.86; H 7.32; N 17.07.

5. Quantitative determination of the cyclohexenylcyanacetic ester. Exactly 5.0 ml of 1N aqueous ammonia was added (from a buret) to a quantity of cyclohexenylcyanacetic ester (0.2-0.3 g) placed in a conical flask with a ground-glass stopper. The mixture was chilled in a salt-ice mixture, and 5 ml of alcohol was added, after which the whole was shaken up and allowed to stand for 12 hours. Then the ammonia was back-titrated with 0.1N hydrochloric acid in the presence of methyl red. Before titration the flask was again chilled to prevent the loss of any ammonia. A blank test was run in parallel.

The method is also suitable for determining the cyanacetic acid, the time the mixture stands then being cut to 1-1.5 hours.

The results of our determination of the cyanacetic and cyclohexenylcyanacetic esters, as well as of artificial mixtures of cyclohexenylcyanacetic and methylcyclohexenylcyanacetic esters, are tabulated in Tables 1, 2, and 3.

TABLE 1
Determination of Cyanacetic Ester [1]

Test No.	Grams of cyanacetic ester used	Ml of 0.1N hydrochloric acid	% of cyanacetic ester found
1	0.1048	9.25	99.7
2	0.1782	16.65	99.2
3	0.2290	20.20	99.6
4	0.3680	32.30	99.1
5	0.3926	34.50	99.3
6	0.1800	15.75	98.9
7	0.2192	19.40	99.5
		Average	99.3

[1]) B.p. 96-97° at 15-16 mm. Ester content: 1) 99.8% by saponification number; 2) 99.9% by nitrogen content (Kjeldahl).

TABLE 2
Determination of Cyclohexenylcyanacetic Ester [2]

Test No.	Grams of cyclohexenylcyanacetic ester used	Ml of 0.1N hydrochloric acid	% of cyclohexenylcyanacetic ester found
1	0.2570	12.70	95.3
2	0.2600	12.70	94.2
3	0.2312	11.40	95.1
4	0.3192	15.60	94.3
5	0.2230	10.90	94.3
		Average	94.6

[2]) B.p. 165-167° at 15-16 mm. Ester content: 1) 95.4% by saponification number; 2) 95.8% by nitrogen content (Kjeldahl).

The figures in Table 3 indicate that the methylcyclohexenylcyanacetic ester hardly reacts with ammonia at all. The deviations of the experimental values from the quantities used lie within the limits of experimental error, totaling no more than 0.3% abs.

SUMMARY

1. The solid by-product of the synthesis of hexenal has been isolated and identified as 3-methyl-4-imino-5-cyclohexenylbarbituric acid.

TABLE 3

Determination of Cyclohexenylcyanacetic Ester in Artificial Mixtures Composed of Cyclohexenylcyanacetic Ester (B.p. 165-167° at 15-16 mm; Ester Content 94.6%) and Methylcyclohexenylcyanacetic Ester (B.p. 136-138° at 14-15 mm; Ester Content 97%)

Test No.	Grams of cyclohexenyl-cyanacetic ester used	Grams of methylcyclohex-enylcyanacetic ester used	Ml of 0.1N hydrochloric acid	% of cyclohex-enylcyanacetic ester found	% of cyclohexenyl-cyanacetic ester used
1	0.3690	0.2592	18.10	55.1	55.3
2	0.1764	0.3276	8.70	33.3	33.1
3	0.1712	0.3142	8.35	33.2	33.3
4	0.1028	0.4040	5.10	19.4	19.2
5	0.0422	0.3424	2.10	10.2	10.4
6	0.0608	0.7942	3.00	7.0	6.7
7	–	0.4272	0.05	0.2	0.0
8	0.0384	0.7206	1.90	4.8	4.7
9	–	0.2600	0.05	0.4	0.0
10	–	0.4454	0.05	0.2	0.0

2. It has been found that 3-methyl-4-imino-5-cyclohexenylbarbituric acid is produced by the condensation of cyclohexenylcyanacetic ester with acetylmethylurea.

3. It has been found that the methylcyclohexenylcyanacetic ester that contains no cyclohexenyl cyanacetic ester does not yield a solid by-product during its condensation with acetylmethylurea.

4. A method is suggested for preparing pure methylcyclohexenylcyanacetic ester, involving the processing of the technical ester mixture with aqueous ammonia.

5. A method has been developed for quantitatively determining cyclohexenylcyanacetic ester when methylcyclohexenylcyanacetic ester is present.

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Leningrad Research Institute of Pharmaceutical Chemistry

TABLE 1

Hydrolysis of Secondary Amines Over Al_2O_3 at 400°

Secondary amines	Hydrolysis products				Remarks
	Unsaturated hydrocarbons or their dibromides	Yield	NH_3 or primary amines	Yield	
Diethylamine	Ethylene bromide	25%	NH_3	54%	Dibromobutane and 1,2,3,4-tetrabromobutane were also found
Dibutylamine	1,2-Dibromobutane	48.5%	NH_3 Monobutylamine	73% Picrate	–
Dicyclohexylamine	Cyclohexene	70%	–	–	–
Ethylamine	Ethylene bromide	37%	Aniline	58%	12% of the unchanged ethylaniline
Phenylcyclohexylamine	Cyclohexene	66%	Aniline	57%	Traces of diphenylamine
Phenylcyclohexylamine + H_2O	Cyclohexene	54.5%	Aniline	78%	–

The yield of the N-alkyl or N-aryl pyrrolidines (Table 2) when they are synthesized from furanidine and secondary amines is inversely proportional to the degree of hydrolysis of the secondary amine, apparently because it is mainly the hydrolysis of the secondary amine that occurs above the catalyst.

TABLE 2

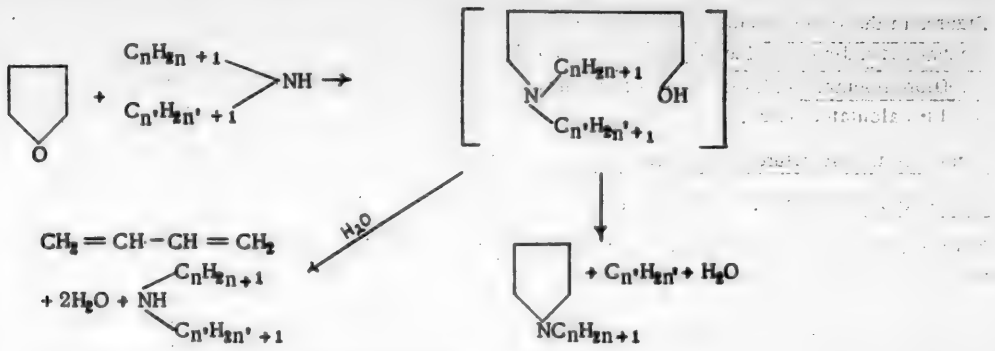
Reaction of Furanidine with Secondary Amines over Al_2O_3 at 400°

Secondary amines	Reaction products				Remarks
	N-substituted pyrrolidines	Yield	Unsaturated hydrocarbons or their dibromides	Yield	
Diethylamine [1]	N-Ethylpyrrolidine	29%	Ethylene bromide	9.4%	–
Dibutylamine	N-Butylpyrrolidine and pyrrolidine	4.5% Traces	1,2-Dibromobutane	21.5%	NH_3 – 48%
Dicyclohexylamine	N-Cyclohexylpyrrolidine	Traces	Cyclohexene	70%	–
Ethylaniline [2]	N-Phenylpyrrolidine	11%	Ethylene bromide	60%	55% aniline
Phenylcyclohexylamine [3]	N-Phenylpyrrolidine	6%	Cyclohexene	60%	59% aniline

The data in Tables 1 and 2 indicate that the hydrolysis of secondary amines is not increased appreciably when these amines are reacted with furanidine (except in the case of ethylaniline). It has also been found that diphenylamine does not react with furanidine: 75% of the unchanged diphenylamine was recovered from the catalyzate produced when a mixture of furanidine and diphenylamine was passed over Al_2O_3 at 400°. No N-phenylpyrrolidine was produced. Thus, a secondary amine whose hydrolysis is hampered does not react with furanidine.

Lastly, if the reaction were to follow the second schema, the hydrolysis of the intermediate tert-aminobutanol ought to result in the production of more divinyl than is produced by the dehydration of pure furanidine over alumina (or by the hydrolysis of a 4-alkylaminobutanol-1), since it is easier to hydrolyze tertiary amines than secondary or primary amines: (see diagram top of next page).

The amount of divinyl produced when furanidine was passed over alumina at 400° proved to be just as small, however, as when furanidine was reacted with ethylamine or diphenylamine. We, therefore, conclude, contrary to our previous position, that when furanidine is reacted with secondary amines over Al_2O_3 at 400°, the secondary amine is first hydrolyzed, the resulting primary amine (I and II) reacting with the furanidine, i.e., that the first of the schemas set forth above for the mechanism involved in this reaction is correct.



EXPERIMENTAL

I. Hydrolysis of Secondary Amines over Al_2O_3

1. Hydrolysis of diethylamine. a) 10 grams of diethylamine was passed over alumina at 400° in a current of nitrogen at a rate of 6-8 drops per minute. The catalyzate was collected in a well-chilled receiver, which was connected to a wash bottle containing dilute hydrochloric acid and two wash bottles containing bromine. Three ml of catalyzate was collected in the receiver. Evaporating the hydrochloric acid solution yielded 4.3 g of ammonium chloride. The bromine was driven off from the contents of the bromine bottles, which were then washed with water, dried with calcium chloride, and double-distilled, yielding the following two fractions: b.p. 130-135°—5 g; and b.p. 135-160°—4.3 g.

b) A mixture of 10 g of diethylamine and 2.5 ml of water was passed over alumina under the same conditions. This yielded: 4 g of moist catalyzate, 4 g of ammonium chloride, 14 g of a dibromide with a b.p. of 129-135°, and 4.7 g of a dibromide with a b.p. of 135-155°.

c) Processing a mixture of 14 g of diethylamine and 4 ml of water under the same conditions yielded: 5 ml of moist catalyzate, 5 g of ammonium chloride, 23 g of a dibromide with a b.p. of 129-135°; and 6.2 g of a dibromide with a b.p. of 135-160°. The residue left after the dibromides had been driven off crystallized; its m.p. was 117-118° after recrystallization from petroleum ether, and it proved to be 1,2,3,4-tetrabromobutane. Its mixed melting point with pure 1,2,3,4-tetrabromobutane was 117-117.5°, exhibiting no depression.

Figures in the literature for 1,2,3,4-tetrabromobutane: m.p. 116-119° [4]; m.p. 116-117° [5].

Drying and distilling the combined catalyzates of all the runs yielded 1.8 g of unchanged diethylamine, with a b.p. of 55-60°. A total of 13.3 g of ammonium chloride was collected from all the runs (54.4% of the theoretical).

The respective dibromides (from three runs) were mixed together, yielding the following compounds after fractionation into a column with an efficiency of 18 theoretical trays:

Ethylene bromide (44 g—25% of the theoretical): b.p. 128.5-129.5° (742 mm); n_D^{20} 1.5384; d_4^{20} 2.1695; MR_D 27.11; calculated 26.96;

High-boiling bromide (2.5 g): b.p. 157.5-159° (742 mm); n_D^{20} 1.5160; d_4^{20} 1.8282.

43.186 mg substance: titration of 0.1 part by weight consumed 2.007 mg of a 0.02N solution of $AgNO_3$.
28.720 mg substance: titration of 0.1 part by weight consumed 1.332 ml of a 0.02N solution of $AgNO_3$.
Found %: Br 74.30, 74.15. $C_2H_4Br_2$. Calculated %: Br 74.02.

The analysis data and the constants indicate that this dibromide is apparently dibromobutane.

Hence, passing diethylamine over alumina at 400°, either by itself or mixed with water, cleaves it, yielding ethylene (25% of the theoretical) and ammonia (54% of the theoretical).

2. Hydrolysis of dibutylamine. A mixture of 15 g of n-dibutylamine (b.p. 159°) and 2 ml of water was passed over Al_2O_3 at 400° in a current of nitrogen at a rate of 6-8 drops per minute. The reaction products were collected and isolated as described above. The following reaction products were recovered:

n-Butylamine (0.8 g), identified by preparing its picrate, m.p. 149-150°.

Figures in the literature for n-butylamine: picrate melting point 151° [6].

Unchanged n-dibutylamine (1.0 g), b.p. 157-159°.

1,2-Dibromobutane (24.4 g—48.6% of the theoretical): b.p. 54.5-55.5° (16 mm); d_4^{20} 1.8011; n_D^{20} 1.5147; MR_D 36.14; calculated 36.20.

Figures in the literature for 1,2-dibromobutane: d_4^{20} 1.8204 [7]; b.p. 166.3° [8]; n_D^{20} 5171 [9];

Ammonium chloride (4.5 g—72.6% of the theoretical).

Thus, the hydrolysis of dibutylamine yields butene-1 (48.6% of the theoretical); ammonia (72.6% of the theoretical); and a slight amount of n-butylamine.

3. Hydrolysis of dicyclohexylamine. 13.5 grams of dicyclohexylamine, with a b.p. of 123-124° (17 mm), was passed over Al_2O_3 at 400° in a current of nitrogen at the rate of 8-10 drops per minute. This yielded 10.8 g of catalyzate, distillation of which (after drying) yielded 8.5 g of cyclohexene (70% of the theoretical).

B.p. 82-83° (758 mm); n_D^{20} 1.4450; d_4^{20} 0.8113; MR_D 27.17; calculated 27.24.

Figures in the literature for cyclohexene: b.p. 84° (763 mm); d_4^{20} 0.8112; n_D^{20} 1.4469 [10].

4. Hydrolysis of ethylaniline. 46 grams of ethylaniline, b.p. 84.4-84.8° (10 mm), was passed (in 23-g portions) over Al_2O_3 at 400° in a current of nitrogen at the rate of 6-8 drops per minute. The receiver was connected to a wash bottle containing bromine. Drying the catalyzate and double-distilling it in vacuo yielded:

Aniline (16.7 g—58.2% of the theoretical): b.p. 72-73° (11 mm); n_D^{20} 1.5827; m.p. of acetanilide 114-115°.

Ethylaniline (5.5 g—12% of the amount placed in reaction).

The contents of the flask containing bromine yielded 26.6 g of ethylene bromide (37.0% of the theoretical), b.p. 130.5-131.5° (760 mm); n_D^{20} 1.5345.

Thus, ethylaniline is hydrolyzed substantially, yielding ethylene and aniline.

5. Hydrolysis of phenylcyclohexylamine. a) 14 g of phenylcyclohexylamine, with a b.p. of 137.5-139.5° (8 mm), was passed over alumina at 400° in a current of nitrogen at the rate of 6-8 drops per minute. This yielded 12 ml of catalyzate. The ether extract of the catalyzate was dried with potash, and the ether driven off, the residue yielding:

Cyclohexene (4.3 g—66% of the theoretical): b.p. 81.5-82.5 (750 mm); n_D^{20} 1.4428; d_4^{20} 0.8056; MR_D 27.06; calculated 27.24;

Aniline (4.2 g—57% of the theoretical): b.p. 64-65° (8 mm); n_D^{20} 1.5820; m.p. of acetanilide 114°.

Diphenylamine (0.3 g), whose melting point was 52.5° after double recrystallization from petroleum ether. Its mixed melting point with pure diphenylamine was 52-52.5°, exhibiting no depression.

b) A mixture of 12 g of phenylcyclohexylamine and 1.2 ml of water was passed over Al_2O_3 under the conditions described above. This yielded 10 ml of catalyzate, the customary processing yielding:

Cyclohexene (3 g—54.5% of the theoretical): b.p. 82-83° (762 mm); n_D^{20} 1.4442; d_4^{20} 0.8008; MR_D 27.26;

Aniline (5 g—78.0% of the theoretical): b.p. 74-76° (14 mm); n_D^{20} 1.5842.

Thus, hydrolyzing phenylcyclohexylamine by placing it in contact with Al_2O_3 yields aniline, cyclohexene, and traces of diphenylamine.

II. Reaction of Furanidine with Secondary Amines.

1. Reaction of furanidine with n-dibutylamine. a) A mixture of 10 g of furanidine and 18 g of n-dibutylamine (1:1) was passed over Al_2O_3 at 400° in a current of nitrogen at the rate of 6-8 drops per minute. This yielded 14 ml of catalyzate. The receiver was connected to a wash bottle containing dilute hydrochloric acid, followed by two wash bottles containing bromine. The usual processing of the bromides yielded:

1,2-Dibromobutane [1] (22.3 g—21.5% of the theoretical): b.p. 163-164° (750 mm); n_D^{20} 1.5137; d_4^{20} 1.7888; MR_D 36.33; calculated 36.20.

1) In distilling the dibromide we secured 11.7 g of first runnings with a b.p. of 140-163° (750 mm), which were apparently a mixture of 1,2-dibromobutane and 1,2-dibromopropane, the latter being formed from propylene, a decomposition product of the furanidine [1].

1,2,3,4-Tetrabromobutane (0.6 g): m.p. 116-117°.

b) A mixture of 7.5 g of furanidine and 13 g of n-dibutylamine was passed over Al_2O_3 under the same conditions, yielding 7.5 ml of catalyzate. The receiver was connected to a wash bottle containing 250 ml of 1.138N hydrochloric acid; titration with a sodium hydroxide solution established that 0.787 g of ammonia (48% of the theoretical) was evolved during the reaction.

The catalyzates of Runs (a) and (b) were combined, dried, and distilled, yielding:

Pyrrolidine (0.5 g of a fraction with a b.p. of 82-90°), whose picrate melting point was 111-112° (after recrystallization from alcohol); the mixed melting point with the picrate of pure pyrrolidine was 111-112°, exhibiting no depression.

N-butylpyrrolidine (1.4 g—4.5% of the theoretical): b.p. 151-155°; picrate melting point 124-124.5° (from alcohol).

Figures in the literature for pyrrolidine: Yu. K. Yuryev [11]: b.p. 85.8-86.8°; picrate melting point 112°; for N-butylpyrrolidine: Yu. K. Yuryev [11]: b.p. 154.5-155.5° (748.5 mm); n_D^{20} 1.4408; d_4^{20} 0.8143; picrate melting point 124°.

Thus, the reaction of furanidine with n-dibutylamine involves substantial hydrolysis of the dibutylamine, resulting in the production of butene-1, in addition to the formation of negligible quantities of N-butylpyrrolidine and pyrrolidine.

2. Reaction of furanidine with dicyclohexylamine. A mixture of 5 g of furanidine and 12 g of dicyclohexylamine was passed over Al_2O_3 at 400° under the conditions described above. The ether extract was dried with fused potassium hydroxide and the ether driven off, yielding:

Cyclohexene (7.6 g—70.0% of the theoretical): b.p. 81-83° (760 mm); n_D^{20} 1.4460; d_4^{20} 0.8107; MR_D 27.02;

N-cyclohexylpyrrolidine (0.3 g): b.p. 65-68° (5 mm); picrate melting point (from alcohol): 163-164°.

Figures in the literature for N-cyclohexylpyrrolidine: Yu. K. Yuryev [11]: b.p. 79° (8 mm): n_D^{20} 1.4888; d_4^{20} 0.9135; picrate melting point 164.5°.

No pyrrolidine was found.

Thus, only a negligible amount of N-cyclohexylpyrrolidine is produced when furanidine is reacted with dicyclohexylamine, the principal reaction product being cyclohexene (70% of the theoretical yield).

3. Reaction of furanidine with diphenylamine. A solution of 23.4 g of diphenylamine in 10 g of furanidine was passed over Al_2O_3 at 400° in a current of nitrogen at the rate of 6-8 drops per minute. The gases evolved were absorbed in bromine. The catalyzate, which crystallized in the receiver, was dissolved in ether and dried with fused alkali, the ether driven off, and the residue distilled in vacuo. This yielded 0.5 g of a fraction with a b.p. of 60-120° (5 mm) and 17.5 g of a fraction with a b.p. of 125-130° (5 mm).

The second fraction consisted of the unchanged diphenylamine (74.8% of the amount used for the reaction), which had an m.p. of 51-52° after recrystallization from petroleum ether. The fraction with a b.p. of 60-120° (5 mm) yielded acetanilide with an m.p. of 113° and a picrate, which had an m.p. of about 170° (with decomposition) after recrystallization from alcohol, evidence that this fraction contained aniline.

The contents of the flask containing bromine yielded 4.5 g of 1,2-dibromopropane (15.1% of the theoretical): b.p. 139-141° (759 mm); n_D^{20} 1.5210; d_4^{20} 1.9225; MR_D 31.98; calculated 31.58.

Recrystallization frompetroleum ether of the residue left after the 1,2-dibromopropane had been distilled yielded 0.3 g of 1,2,3,4-tetrabromobutane with an m.p. of 116-117°.

Thus, no N-phenylpyrrolidine is produced when furanidine is reacted with diphenylamine. The following reaction products were found: negligible amounts of aniline and propylene, and traces of divinyl, 75% of the diphenylamine being recovered unchanged.

4. Formation of divinyl when furanidine is reacted with ethylamine. A mixture of 6 g of ethylamine and 7.5 g of furanidine was passed over Al_2O_3 at 400°. A total of 1886 ml of gas (NTP) was collected. The gases contained 1.3% of divinyl (determined in a Korotkov apparatus [12]), in other words, furanidine is only 0.9%

dehydrated over Al_2O_3 to yield divinyl.

5. Formation of divinyl when furanidine is reacted with diphenylamine. A solution of 13 g of diphenylamine in 6 g of furanidine was passed over Al_2O_3 at 400°, yielding 1447 ml of gas (NTP). The gas contained 1% of divinyl, so that furnidine is only 0.7% dehydrated to yield divinyl (in the presence of diphenylamine).

III. Behavior of Furanidine over Al_2O_3 at 400°.

a) 10 g of furanidine was passed over Al_2O_3 at 400° in a current of nitrogen at the rate of 6-8 drops per minute. The gases evolved were absorbed in bromine. The customary processing of the contents of the bromine-filled bottles yielded:

1,2-Dibromopropane (9 g—32.2% of the theoretical): b.p. 139-140° (757 mm); n_D^{20} 1.5210; d_4^{20} 1.9323; MR_D 31.44 and 0.2 g of 1,2,3,4-tetrabromobutane with a m.p. of 117°.

b) When 10 g of furanidine was passed over the catalyst under the same conditions, we collected 3165 ml of gas (NTP), 871 ml of which was nitrogen. The composition of the gas (without the nitrogen) was as follows: 3.6% CO_2; 73% unsaturated hydrocarbons; 1.1% oxygen; 7% carbon monoxide; 6.8% hydrogen; and 8.5% saturated hydrocarbons.

c) 5.7 grams of furanidine yielded 990 ml of gas (NTP) when passed over Al_2O_3 at 400°. The divinyl totaled 1.42% (analysis in a Korotkov apparatus [12]) i.e., furanidine is 0.8% dehydrated over Al_2O_3 at 400° to yield divinyl.

Thus, furanidine is decomposed over Al_2O_3 at 400°, the principal products being propylene, carbon monoxide, carbon dioxide, and hydrogen; a small amount of divinyl is also produced.

SUMMARY

The present paper demonstrated that when furanidine is reacted with secondary amines over Al_2O_3 at 400°, the secondary amine is first hydrolyzed, the resulting primary amine then reacting with the furanidine.

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The N.D. Zelinsky Laboratory of Organic Chemistry, Moscow State University

SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

XIX. POLAROGRAPHIC INVESTIGATION OF PYRROLESULFONIC ACIDS

A. P. Terentyev, L. A. Yanovskaya, and Ev. A. Terentyeva

When some pyrroles, such as 1- and 2-acetylpyrrole, and 1-phenylpyrrole, are sulfonated with pyridine sulfotrioxide, beta sulfo acids are produced as well as the alpha acids [1,2]. We needed a method that would enable us to determine the isomer present in a small quantity of sulfo acid and to establish the individuality of a substance or the existence of a mixture, in order to be able to analyze the reaction products of the sulfonation of pyrroles.

None of the existing chemical methods was able to meet our needs. Although oxidation of the barium salts of pyrrolesulfonic acid with a chromic acid mixture makes it possible, in general, to determine the acid's structure and even to decide whether we are dealing with an individual substance or a mixture of isomers, the method is not very precise: possibly not all the oxidation products being collected when small quantities are being used, especially when one of the isomers predominates.

The method of solubility and lixiviation that we have employed in the past to investigate the sulfonation products of pyrrole itself [3], might serve our purpose. But this method of determining the isomers in a mixture requires that we first have the individual substances. It is not always easy to separate a mixture of isomers, the procedure requiring comparatively large quantities of the material and considerable time. In the light of these considerations we rejected this procedure.

Reviewing the entire arsenal of physicochemical methods, we were attracted to the method of polarography, which has been more and more widely utilized in organic chemistry to solve diverse problems, particularly in research on tautomerism and isomerism.

We decided to investigate the polarographic behavior of pyrrolesulfonic acids. In our research we made use of a visual polarographic setup. The rate of mercury discharge was kept constant at one drop in 5 seconds. The potentials were measured against a calomel subsidiary reference electrode with an accuracy of 0.002 volt. The electrolyte used was a half-normal solution of potassium chloride.

We found that the pyrrolesulfonic acids (in the form of their barium salts) are not reduced at a mercury dropping electrode. This forced us to attempt the polarographic oxidation of pyrrolesulfonic acids. Our very first tests showed that pyrrolesulfonic acids are readily oxidized at a mercury dropping electrode, setting up distinct polarographic waves. The present paper is a report on the results we obtained in our study of the polarographic oxidation of pyrrolesulfonic acids.

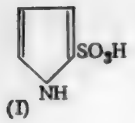
As our tests showed electrolytic oxidation is smoothest in slightly hydrochloric acid media (pH 4.2-4.7). When strongly acid media (pH below 3.7) were employed, maxima appeared on the polarographic curves that were hard to eliminate, thus interfering with measurement of the polarographic waves. Polarography in alkaline media (pH above 9) indicated that it is hard to oxidize pyrrolesulfonic acids under these conditions. The polarographic wave is indistinct in neutral media.

A single procedure was employed in all instances: a sample of the thoroughly purified barium salts of pyrrolesulfonic acids was dissolved in a previously prepared solution of 0.5N KCl–0.003N HCl, in a measuring flask, to make the concentration of the substance about 0.003N (this ensured the optimum solution pH).

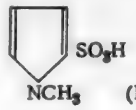
Electrolytic oxidation of pyrrolesulfonic-2 acid (I). The barium salt of pyrrolesulfonic-2 acid used in polarography was recrystallized four times from a water-alcohol mixture.

At a mercury dropping electrode pyrrolesulfonic-2 acid produces a single polarographic wave, the height of which is easily measured. The polarogram is shown in Fig. 1. The half-wave oxidation potential is 0.022 volt.

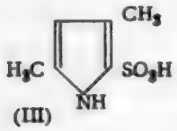
We recorded the polarograms of some other alpha sulfo acids of known structure, in addition to the pyrrolesulfonic-2 acid.


(I)

Electrolytic oxidation of 1-methylpyrrolesulfonic-2 acid (II). The barium salt we used for oxidation was recrystallized twice from a water-alcohol mixture. 1-Methylpyrrolesulfonic-2 acid exhibits a single fully developed wave (Fig. 2). The oxidation half-wave potential is 0.018 volt.


(II)

Electrolytic oxidation of 2,4-dimethylpyrrolesulfonic-5 acid (III). The barium salt of 2,4-dimethylpyrrolesulfonic-5 acid produces a single wave (Fig 3), with a half-wave oxidation potential of 0.015 volts, after thorough crystallization from a water-alcohol mixture and washing with ether.


(III)

Thus, pyrrole sulfo acids with the sulfo group in the alpha position are readily oxidized at a mercury dropping electrode and have half-wave potentials that are closely alike. One cannot fail to note that the accumulation of methyl groups lowers the potential somewhat, i.e., facilitates oxidation. This behavior rigorously conforms to the chemical properties of the pyrroles.

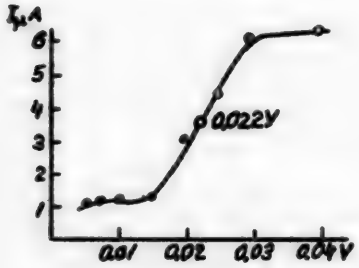


Fig. 1

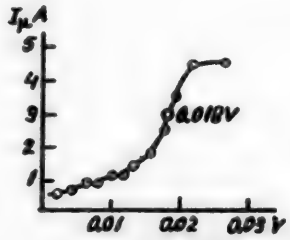


Fig. 2

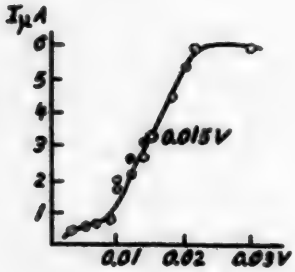


Fig. 3

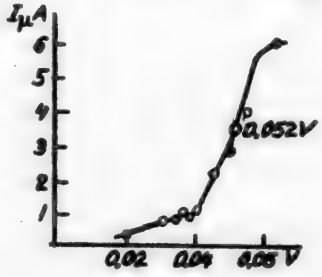
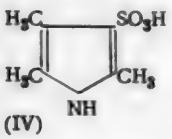


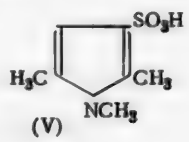
Fig. 4

We investigated the behavior of pyrrole sulfo acids with the sulfo group in the beta position by plotting the polarograms of the barium salts of 2,4,5-trimethylpyrrolesulfonic-3 and 1,2,5-trimethylpyrrolesulfonic-3 acids.

Electrolytic oxidation of 2,4,5-trimethylpyrrolesulfonic-3 acid (IV). The barium salt of 2,4,5-trimethylpyrrolesulfonic-3 acid was purified by repeated reprecipitation from an alocholic solution of ether.


(IV)

The polarogram exhibits a single wave (Fig. 4), with an oxidation half-wave potential of 0.052 volt.


(V)

Electrolytic oxidation of 1,2,5-trimethylpyrrolesulfonic-3 acid (V). Purifying the barium salt of 1,2,5-trimethylpyrrolesulfonic-3 acid required its reprecipitation from alcohol with ether no less than four or five times. The wholly pure salt exhibits a single wave and a half-wave oxidation potential of 0.044 volt (Fig. 5).

Comparing the alpha and the beta pyrrolesulfonic acids reveals a marked difference in their polarographic behavior; the beta pyrrolesulfonic acids displaying much higher oxidation potentials.

The existence of this appreciable difference in potential led us to hope that it would be possible to discriminate between alpha and beta acids in a mixture. To test this, we prepared an artificial mixture of the barium salts of pyrrolesulfonic-2 acid (I) and 2,4,5-trimethylpyrrolesulfonic-3 acid (IV), using approximately equal volumes of the ready solutions, and then polarographed the mixture. We found that the polarographic curve exhibited two distinct curves with half-wave oxidation potentials of 0.021 and 0.044 volt respectively (Fig. 6), i.e., lying within the potential regions of the pure original salts.

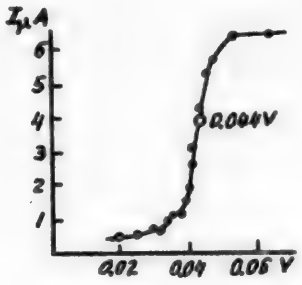


Fig. 5

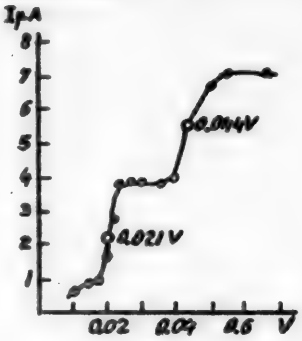


Fig. 6

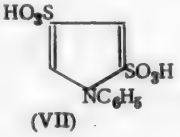
Thus, we can actually discriminate between alpha and beta pyrrolesulfonic acids polarographically in a mixture of the acids.

We then turned to a polarographic investigation of the barium salts that had proved to be heterogeneous upon chemical analysis, or which we might suspect were heterogeneous. We began by polarographing the barium salts of the sulfo acids of 1-phenylpyrrole, 1-(p-nitrophenyl)-pyrrole, 1-o-tolylpyrrole, and 1-phenyl-2-methylpyrrole.

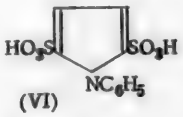
Electrolytic oxidation of 1-phenylpyrrolesulfonic acid. There are two distinct curves on the polarization curve plotted for the polarographic oxidation of 1-phenylpyrrolesulfonic acid. The half-wave oxidation potentials were 0.026 and 0.052 volt, values that lie in the range of the respective alpha and beta pyrrolesulfonic acids. These findings justified us in concluding that the 1-phenylpyrrole sulfonic acid under test is not an individual substance, but rather a mixture of the barium salts of at least two acids: 1-phenylpyrrolesulfonic-2 and 1-phenylpyrrolesulfonic-3 acids. This was a beautiful confirmation of the results of chemical analysis obtained by oxidizing 1-phenylpyrrolesulfonic acid with a chromic acid mixture.

These findings likewise dispel any doubt concerning the possible existence of a third isomer in the mixture, with the sulfo group in the benzene ring, for such an isomer would have to have its own characteristic oxidation potential, and the polarogram would therefore exhibit a third wave. The oxidation potential of a sulfo acid with the sulfo group in the benzene ring would obviously have to be much lower than that of acids in which the sulfo group is attached to the pyrrole ring, inasmuch as the negative sulfo group radical stabilizes the pyrrole ring only when it is attached to that ring itself. The presence of a sulfo group in the phenyl ring would hardly affect the molecule's resistence to oxidation.

Electrolytic oxidation of 1-phenylpyrrolesulfonic acid (VI) and (VII). This acid likewise exhibits two waves in its polarogram (Fig. 7), with half-wave oxidation potentials of 0.20 and 0.042 volt, lying in the ranges that are typical of alpha and beta sulfo acids. We may conclude from a comparison of these findings with the results of our oxidation of 1-phenylpyrrolesulfonic acid that we have here a mixture of the barium salts of isomeric sulfo acids, one obviously possessing the structure of 1-phenylpyrroledisulfonic-2,5 acid (VI). The most likely structure of the other acid is 1-phenylpyrroledisulfonic-2,4 acid (VII). It is impossible to use this method to resolve the problem of the existence of isomeric sulfo acids with one of the sulfo groups in the benzene ring, since the oxidation potential of such acids would obviously be

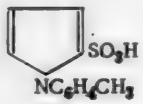


(VII)



(VI)

governed by the position of the other sulfo group at the alpha or beta position in the pyrrole ring.



(VIII)

Electrolytic oxidation of 1-(p-nitrophenyl)-pyrrolesulfonic acid. The polarogram of the barium salt of 1-(p-nitrophenyl)-pyrrolesulfonic acid has two waves, the half-wave oxidation potentials being 0.019 and 0.050 volt, respectively. Hence, this salt is also a mixture of isomeric salts of the alpha and beta sulfo acids.

Electrolytic oxidation of 1-o-tolylpyrrolesulfonic acid (VIII). By analogy with the 1-phenylpyrrolesulfonic acid we might suppose that 1-o-tolylpyrrolesulfonic acid is also a mixture. We tested this assumption by oxidizing the barium salt of 1-o-tolylpyrrolesulfonic acid with a mercury dropping electrode. The polarization curve exhibited only one wave, however, with half-wave oxidation potential of 0.024 volt (Fig. 8). This proves that this is an individual sulfo acid with the sulfo group in the alpha position, a conclusion that is borne out by the results of oxidizing 1-o-tolylpyrrolesulfonic acid with a chromic acid mixture, N-o-tolylmaleinimide being the sole product.

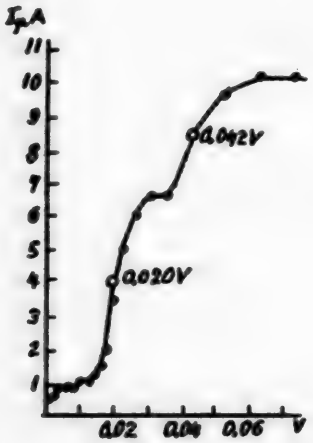


Fig. 7

Electrolytic oxidation of 1-phenyl-2-methylpyrrolesulfonic acid (IX). The polarogram of the barium salt of 1-phenyl-2-methylpyrrolesulfonic acid likewise exhibits only a single wave (Fig. 9), its half-wave oxidation potential being 0.019 volt. Hence, this acid is an individual substance, with the structure of 1-phenyl-2-methylpyrrolesulfonic-5 acid. This conclusion agrees with the results of chemical oxidation.

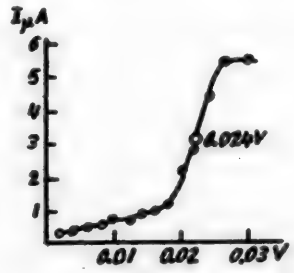
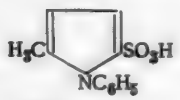


Fig. 8

After plotting the polarograms of the group of N-aryl substitution derivatives of pyrrolesulfonic acids, we turned to the polarographic study of acetylpyrrolesulfonic acids.



(IX)

Electrolytic oxidation of 1-acetylpyrroldisulfonic acid (X) and (XI). There are three distinct waves in the polarogram of 1-acetylpyrroledisulfonic acid (Fig. 10). Two of these waves lie in the potential ranges typical of alpha and beta pyrrolesulfonic acids (0.024 and 0.053 volt).

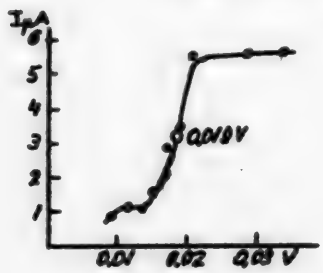


Fig. 9

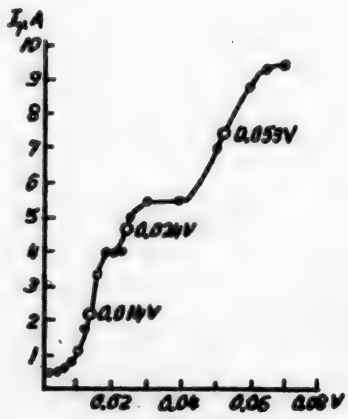
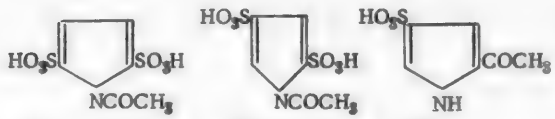


Fig. 10

These findings are evidence that the initial substance contains at least two isomeric acids: 1-acetylpyrroledisulfonic-2,5 (X) and 1-acetylpyrroledisulfonic-2,4 (XI) acid. This conclusion agrees with the results of chemical oxidation. The genesis of the first wave with a half-wave oxidation potential of 0.014 volt is unclear.



(X) (XI) (XII)

Electrolytic oxidation of the 2-acetylpyrrolesulfonic acids produced by sulfonating 2-acetylpyrrole with oleum and pyridine sulfotrioxide (XII). There are two waves visible (Fig. 11) in the polarogram for the oxidation at a mercury dropping electrode of the 2-acetylpyrrolesulfonic acid prepared by sulfonating 2-acetylpyrrole with oleum. The half-wave potentials are 0.015 and 0.055 volt.

The polarogram for the 2-acetylpyrrolesulfonic acid prepared by sulfonating 2-acetylpyrrole with pyridine sulfotrioxide likewise exhibits two waves, with half-wave potentials of 0.017 and 0.053 volt (Fig 12).

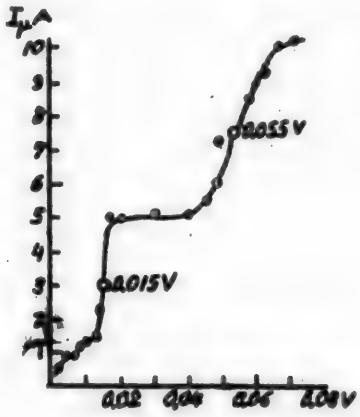


Fig. 11

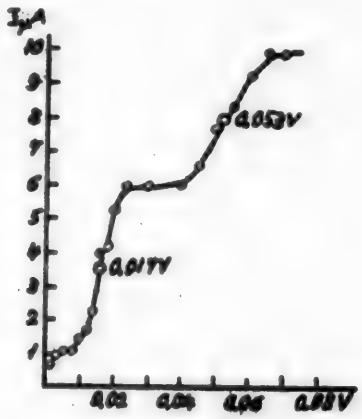


Fig. 12

It is obvious that waves with half-wave potentials of 0.055 and 0.053 volt belong to a 2-acetylpyrrolesulfonic acid with the sulfo group at the beta position (XII). We are not inclined to attribute the presence of a second wave in both of these polarograms to the existence of a second isomer in the original substances, for the polarogram of 1-acetylpyrrolesulfonic acid also exhibits a wave with a half-wave oxidation potential of 0.014 volt, a value that is extremely close to the values of 0.015 and 0.017 volt obtained for 2-acetylpyrrole sulfonic acid.

It should be noted that a certain scattering of the plotted points in the region of the potentials typical of alpha pyrrole sulfo acids is observed in the polarogram of the 2-acetylpyrrolesulfonic acid prepared by sulfonating 2-acetylpyrrole with pyridine sulfotrioxide, which indicates that the alpha isomer may be present as an impurity.

SUMMARY

1. It has been shown that the polarographic oxidation method may be employed to determine the position of the sulfo group in pyrrolesulfonic acids.

2. It has been shown that the alpha and beta pyrrole sulfo acids in a mixture can be determined polarographically.

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Received September 29, 1950 Laboratory of Organic Chemistry, The Lomonosov State University of Moscow

*See Consultants Bureau translation, p. a-591.

**See Consultants Bureau translation, p. 539.

SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

XX. POLAROGRAPHIC INVESTIGATION OF INDOLESULFONIC ACIDS

A. P. Terentyev and L. A. Yanovskaya

The interesting results we had obtained in our study of pyrrolesulfonic acids by the polarographic oxidation method [1], impelled us to apply this method to the indolesulfonic acids.

The experiments were carried out under the same conditions as those described in our preceeding report. We used a visual polarographic setup, the discharge rate of the mercury being one drop every 5 seconds, the electrolyte being a 0.5N solution of potassium chloride, acidulated with hydrochloric acid, and the potentials being measured by comparison with a calomel subsidiary reference electrode. Barium salts of indolesulfonic acids, thoroughly purified by recrystallization from aqueous or water-alcohol solutions, were dissolved in a prepared KCl-HCl mixture, whose composition was such that the resulting solution had a 0.003 N concentration of the indolesulfonic acid and a pH of 4.2-4.7. We began by polarographing alpha indolesulfonic acids.

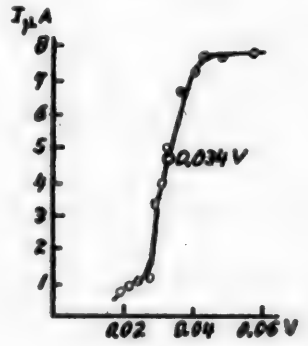


Fig. 1

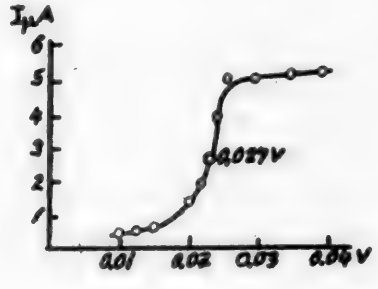
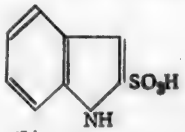


Fig. 2

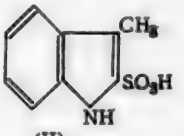
Electrolytic oxidation of indolesulfonic-2-acid (I). This acid was prepared by sulfonating indole at a temperature of 110-120° [2], with pyridine sulfotrioxide that contained no excess of sulfur trioxide. The structure of the acid was established as indolesulfonic-2 acid by reacting it with a fused alkali and hydrolyzing it with hydrochloric acid, the oxindole produced being isolated and identified.



(I)

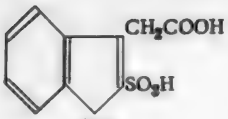
The polarogram (Fig. 1) displayed a single wave with a half-wave oxidation potential of 0.034 volt.

Electrolytic oxidation of 3-methylindolesulfonic-2 acid (II). The barium salt of 3-methylindolesulfonic-2 acid was smoothly oxidized at the mercury dropping electrode, one wave being exhibited by the polarogram. The half-wave oxidation potential was 0.027 volt (Fig. 2).



(II)

Electrolytic oxidation of 2-sulfo-3-indolylacetic acid (III). The polarogram of the barium salt of 2-sulfo-3-indolylacetic acid closely resembled the preceding one. The half-wave oxidation potential was 0.026 volt (Fig. 3).



(III)

Thus, the indolesulfonic acids with the sulfo group in the alpha position are oxidized fairly easily at a mercury dropping electrode. It is worthy of note that the half-wave oxidation potentials of alpha indolesulfonic acids are appreciably higher than the half-wave oxidation potentials of alpha pyrrolesulfonic acids (the half-wave potential of pyrrolesulfonic acid is 0.022 volt, for example, while that of indolesulfonic-2 acid is 0.034 volt). This agrees satisfactorily with the fact that indole compounds are known to be more stable than pyrrole compounds.

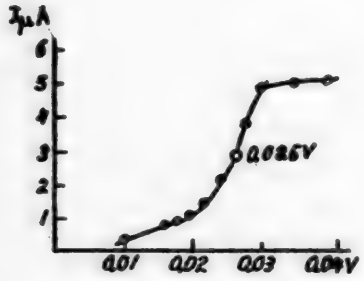


Fig. 3

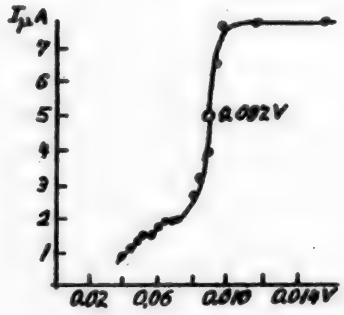
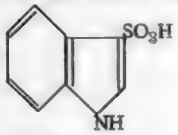


Fig. 4

It should also be pointed out that introducing methyl groups lowers the oxidation potentials of indole sulfo acids somewhat, as we found to be true of alpha pyrrole sulfo acids as well.

We then turned to polarographic investigation of beta indolesulfonic acids.

Electrolytic oxidation of indolesulfonic-3-acid (IV). This acid was prepared by sulfonating indole at a temperature of 130-140° with pyridine sulfotrioxide containing a 0.6% excess of sulfur trioxide. Its structure was established by producing indigo with fused alkali.

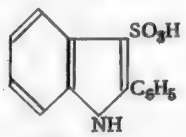


(IV)

The polarogram of the barium salt of indolesulfonic-3 acid exhibits a single wave with a half-wave oxidation potential of 0.092 volt (Fig. 4).

Electrolytic oxidation of 2-phenylindolesulfonic-3 acid (V). The polarogram of 2-phenylindolesulfonic-3 acid exhibits one wave with a half-wage potential of 0.058 volt (Fig. 5).

These findings show that the beta indole sulfo acids have much higher half-wave oxidation potentials than the alpha indole sulfo acids. A similar distinction was found to exist in the pyrrole sulfo acids.



(V)

We also had available a preparation of indolesulfonic-1 acid as its barium salt. We polarographed this sample as well in order to determine the effect of the N position of the sulfo group upon the oxidation potential.

Electrolytic oxidation of indolesulfonic-1 acid (VI). The barium salt of indolesulfonic-1 acid was oxidized smoothly at the mercury dropping electrode, yielding one wave with a half-wave oxidation potential of 0.025 volt (Fig. 6).

It is apparent from these findings that the magnitude of the oxidation potential is largely affected by the position of the sulfo group in the pyrrole ring. The beta indole sulfo acids have the highest potentials (i.e., are hardest to oxidize), while indolesulfonic-1 acid exhibits the lowest oxidation potential. Hence, the magnitude of the half-wave oxidation potential affords an indication of the position of the sulfo group in the indole molecule.

We felt it was also not without interest to make a study of the polarographic behavior of indole sulfo acids in which the sulfo group was not attached to the pyrrole ring.

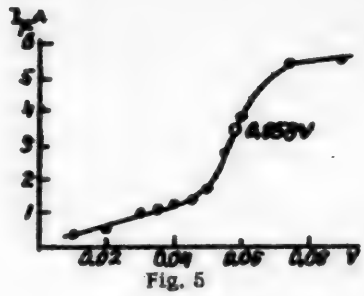


Fig. 5

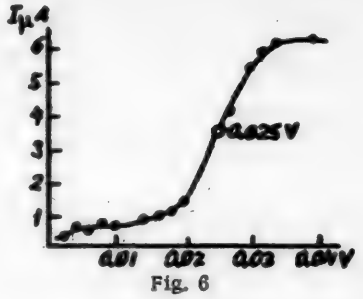


Fig. 6

We had available 2-methylindolesulfonic-5 acid, prepared by sulfonating 2-methylindole with oleum, and 3-indolylmethanesulfonic acid, prepared by methylenesulfonating indole. The position of the sulfo groups in the acids was rigorously established chemically.

Electrolytic oxidation of 2-methylindolesulfonic-5 acid (VII). The polarogram of the barium salt of 2-methylindolesulfonic-5 acid exhibits a single wave, with a half-wave potential of 0.020 volt (Figure 7).

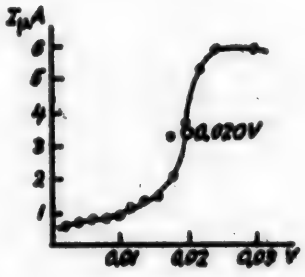


Fig. 7

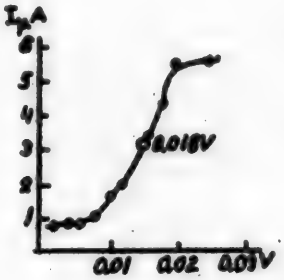


Fig. 8

Electrolytic oxidation of 3-indolylmethanesulfonic acid (VIII). The polarogram of 3-indolylmethanesulfonic acid closely resembles that of the preceding acid. Its half-wave oxidation potential was 0.018 volt (Figure 8).

We see that the half-wave oxidation potentials of both of these sulfo acids are very close together and appreciably lower than the potentials of the α- and β-indole sulfo acids. This indicates that a sulfo group that is not directly attached to a carbon atom in the pyrrole ring does not have much of an effect upon the stability of the indole molecule.

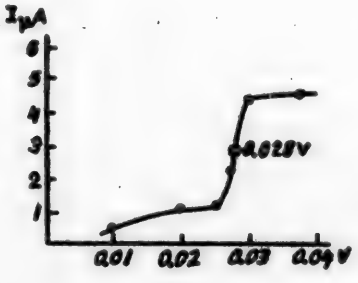


Fig. 9

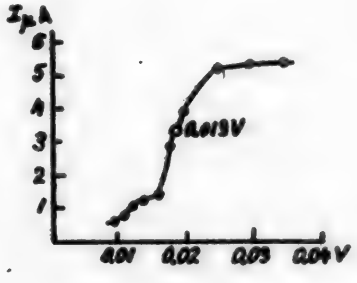
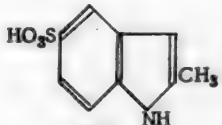


Fig. 10

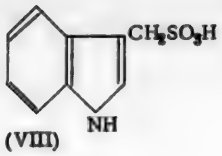
(VI)



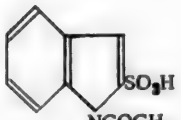
(VII)

On the basis of all these results we had secured, we employed the oxidation polarography method to solve the problem of the structure of several indole sulfo acids: 1-acetylindolesulfonic acid; 3-acetylindolesulfonic acid, prepared by sulfonating 3-acetylindole with oleum; and 2-methylindolesulfonic acid, prepared by sulfonating 2-methylindole with pyridine sulfotrioxide.

Electrolytic oxidation of 1-acetylindolesulfonic acid (IX). The results of a chemical investigation of this acid have shown that it is most probable that the sulfo group enters this compound at the α-position. To resolve all doubts concerning the structure of the acid and its individuality, however, we polarographed its barium salt. The polarogram (Figure 9) exhibited a single wave with a halfwave oxidation potential of 0.028 volt. As has been established in the foregoing examples, potentials of this kind are typical of α-indole sulfo acids. It may be concluded, therefore, that the original substance was the barium salt of 1-acetylindolesulfonic-2 acid.



(VIII)



(IX)

Electrolytic oxidation of 3-acetylindolesulfonic acid (X), prepared by sulfonating 3-acetylindole with oleum. When the barium salt of 3-acetylindolesulfonic acid, prepared by sulfonating 3-acetylindole with oleum, was polarographed, we found a single wave with a halfwave oxidation potential of 0.019 volt (Figure 10). This low potential indicates that the sulfo group is apparently not attached to the pyrrole ring. This is borne out by the results of oxidizing the salt with a chromic acid mixture, in which the sulfo group is not split off. By analogy the most probable structure of the original substance is: 3-acetylindolesulfonic-6 acid (it is in this position that 3-carbethoxyindole is nitrated and brominated).

Electrolytic oxidation of 2-methylindolesulfonic acid (XI), prepared by sulfonating 2-methylindole with pyridine sulfotrioxide. The properties of the methylindolesulfonic acid prepared by sulfonating 2-methylindole with pyridine sulfotrioxide (action on bromine water, hydrolysis by 15% HCl) differed from those of the α- and β-indole sulfo acids. The sulfo group was not attached to the benzene ring, however, as was proved by the results of oxidizing the barium salt with permanganate, the sulfo group being split off completely. Since we wanted to identify the synthesized acid more fully, we polarographed its barium salt. The polarogram (Figure 11) showed a single wave, with a halfwave oxidation potential of 0.017 volt. In the light of all our other results on the electrolytic oxidation of indole sulfo acids, in which the sulfo group was outside the pyrrole ring, we had to assume that the structure of the original substance was 2-indolylmethanesulfonic acid.

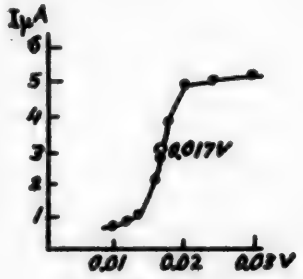
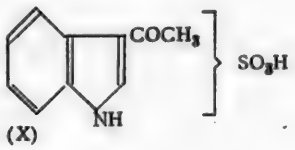
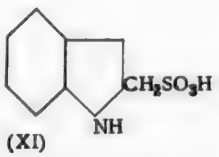


Fig. 11



(X)



(XI)

SUMMARY

It has been shown that the oxidative polarographic method may be employed to determine the position of the sulfo group in indole sulfo acids.

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[1] A. P. Terentyev, L. A. Yanovskaya, and Ev. A. Terentyeva. J. Gen. Chem., 22, 859 (1952); see Consultants Bureau translation, p. 921. cf. also Proc. USSR Acad. Sci., 70, No. 4, 649 (1950).

[2] A. P. Terentyev and L. Tsymbal. Proc. USSR Acad. Sci., 55, 845 (1947).

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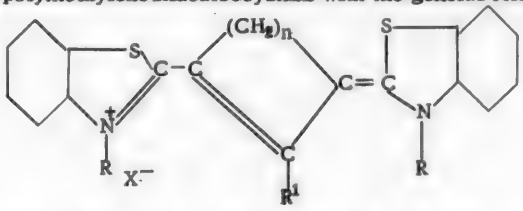
Laboratory of Organic Chemistry,
The Lomonosov State University of Moscow

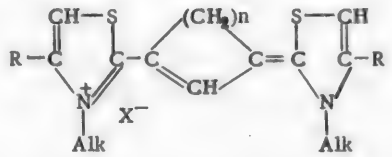
α, γ-POLYMETHYLENETHIAZOLECARBOCYANINS. I.

I. K. Ushenko

The α,γ-polymethylenethiacarbocyanins with the general formula:



(where R = CH_3, C_2H_5, C_6H_5; n = 0, 1, 2, 3, 4, 5, 6; R^1 = H, CH_3, C_2H_5) have been described by us previously [1,2]. The corresponding thiazolecarbocyanins:

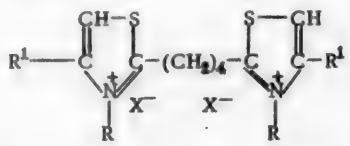


have not been described in the literature. We undertook to synthesize such dyes, containing a five-ring system (n = 2). For this purpose we synthesized two dithiazolylbutanes: α,ω-di-[4-methylthiazolyl-(2)]-butane [3] and α,ω-di[4-phenylthiazolyl-(2)]-butane [4]. These bases were heated in sealed tubes with dimethyl sulfate, and the methyl, ethyl, n-propyl, and n-butyl esters of p-toluenesulfonic acid. The ditertiary salts were isolated and purified in the usual manner.

TABLE 1

No.	R	R^1	X−	Melting point
(I)	CH_3	CH_3	ClO_4	278° (with decomposition)
(II)	C_2H_5	CH_3	ClO_4	268 "
(III)	CH_3	C_6H_5	I	272 "
(IV)	C_2H_5	C_6H_5	I	243 "
(V)	n-C_3H_7	C_6H_5	I	201 "
(VI)	n-C_4H_9	C_6H_5	I	212 "

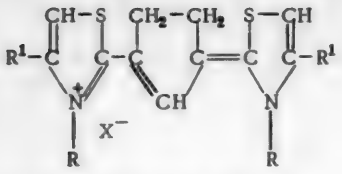
Small quantities of the alkyl p-toluenesulfonates were dissolved in hot water and converted into the corresponding dialkyl perchlorates and dialkyl iodides, listed in Table 1, by the action of an aqueous solution of sodium perchlorate or potassium iodide, respectively.



Heating the dialkyl sulfonates with orthoformic ester in pyridine or with acetic anhydride for a short interval (15-20 minutes) produced thiazolecarbocyanins, turning the solutions an intense blue.

It has been found that the dialkyl p-toluenesulfonates of α,ω-di-[4-phenylthiazoyl-(2)]-butane condense with orthoformic ester much more easily than do the corresponding sulfonates of α,ω-di-[4-methylthiazolyl-(2)]-butane. The synthesized dyes are extremely unstable. They are broken down completely when they stand for a long time in an alcoholic solution, or when attempts are made to isolate them from solution. As the dyes decompose, their solutions turn dark-green and red-purple. We have been able to determine the absorption maxima of these preparations despite their instability.

The absorption maxima of dyes with the general formula of:



in ethyl alcohol are listed in Table 2.

TABLE 2

No.	R	R^1	Absorption maxima (in mμ)
(VII)	C_2H_5	CH_3	595
(VIII)	C_2H_5	C_6H_5	596
(IX)	n-C_3H_7	C_6H_5	600
(X)	n-C_4H_9	C_6H_5	600

We know that unsubstituted 3,3'-diethylthiacarbocyanin iodide (XI) has an absorption maximum at 560 mμ. The λ_{max} of 3,3'-diethyl-8,10-dimethylthiacarbocyanin iodide (XII) is at 601 mμ. Their absorption curves are reproduced in Figure 1.

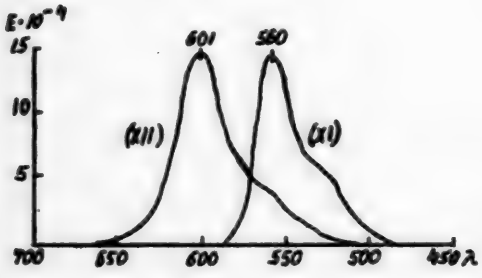


Fig. 1

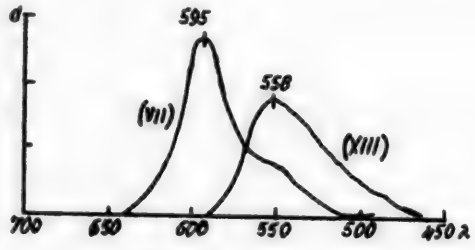


Fig. 2

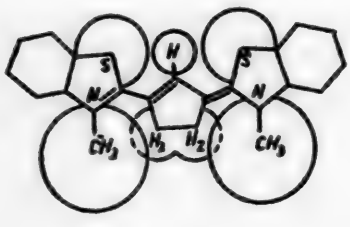


Fig. 3

Thus, closing the five-ring system in the thiacarbocyanins produces a bathochromic effect of 41 mμ.

3,3'-Diethyl-4,4'-dimethylthiazolecarbocyanin iodide (XIII) has an λ_{max} of 556 mμ. The 3,3'-diethyl-4,4'-dimethyl-6,8-dimethylenethiazolecarbocyanin (VII) we have synthesized has an absorption maximum at 595 mμ. The absorption curves of the last two preparations are given in Figure 2.

In this case closing the five-ring system in the thiazolecarbocyanins produces about the same bathochromic effect. Now the question arises: what is responsible for this high stability of α,γ-dimethylenethiazolecarbocyanins? Apparently, closing the five-ring system sets up an obstacle to the coplanarity of the thiazole rings, which is reflected in the light absorption and in the stability of the dye. We had previously observed that color grew deeper and fastness to alkalies and light was diminished in 8,10-dimethylenethiacarbocyanin. The structure of this latter dye is pictured in Figure 3.

It is common knowledge that the thiazolecyanins are, in general, less stable than the thiacyanins [5]. It is not surprising that the introduction of a five-ring system into the thiazolecarbocyanin molecule diminishes the stability of the dye to such an extent that it cannot be recovered from solution.

EXPERIMENTAL*

α,ω-Di-[4-dimethylthiazolyl-(2)]-butane. This base was synthesized from the dithioamide of adipic acid and chloroacetone [3].

α,ω-Di-[4-phenylthiazolyl-(2)]-butane [4]. This was prepared from the dithioamide of adipic acid and bromoacetophenone [4].

Dimethylperchlorate of α,ω-di-[4-methylthiazolyl-(2)]-butane (I). 0.45 g of α,ω-di-[4-methylthiazolyl-(2)]-butane was heated on a boiling water bath for 1 hour with 0.45 g of dimethyl sulfate. The salt was very soluble in water. The reaction product was dissolved in a small quantity of water, boiled with activated charcoal, filtered,

* The experimental work was done in association with L. T. Belykh.

evaporated on a water bath, and thoroughly warmed to 137°. The yield totaled 0.85 g or 35% of the theoretical. 0.35 g of the methylmethyl sulfate was dissolved in a small quantity of water and converted by the action of sodium perchlorate into the dimethyl perchlorate of α-ω-di[4-methylthiazolyl-(2)]-butane. Its m.p. was 268° with decomposition after recrystallization from alcohol.

Found %: Cl 14.29, 14.30. $C_{14}H_{22}O_8S_2Cl_2$. Calculated %: Cl 14.76.

Diethyl perchlorate of α,ω-di-[4-methylthiazolyl-(2)]-butane (II.) 0.55 g of α,ω-di-[4-methylthiazolyl-(2)]-butane was heated with 0.8 g of ethyl p-toluenesulfonate for 6 hours in a sealed tube on an oil bath at 118-120°. The standard procedure was followed in the isolation and purification of the salt. A slightly yellowish solid. The yield was 1.8 g, or 81% of the theoretical. The diethyl perchlorate consisted of white crystals with a m.p. of 278° with decomposition.

Found %: Cl 13.85, 13.96. $C_{16}H_{26}O_8N_2S_2Cl_2$. Calculated %: Cl 13.90.

Dimethiodide of α,ω-di-[4-phenylthiazolyl-(2)]-butane (III). 2 g of the base was heated in a sealed tube on an oil bath at 115-118° for 4 hours with 2 g of methyl p-toluenesulfonate. The transparent aqueous solution of the salt was concentrated on a water bath. Upon cooling large, lustrous, light-greenish crystals, with a m.p. of 216°, settled out. The yield was 2.4 g, or 61% of the theoretical.

Found %: S 17.62, 17.76. $C_{38}H_{40}O_6N_2S_4$. Calculated %: S 17.12.

The dimethiodide of α,ω-di-[4-phenylthiazolyl-(2)]-butane consisted of light-yellow crystals, with a m.p.of 272° after recrystallization from alcohol.

Found %: I 38.07. $C_{24}H_{26}N_2S_2I_2$. Calculated %: I 38.63.

Diethiodide of α,ω-di-[4-phenylthiazolyl-(2)]-butane (IV). 2 g of α,ω-di-[4-phenylthiazolyl-(2)]-butane was heated in a sealed tube on an oil bath at 130-135° for 8 hours with 2 g of ethyl p-toluenesulfonate. The sulfonate yield was 2.15 g, or 52% of the theoretical. The diethiodide of α,ω-di-[4-phenylthiazolyl-(2)]-butane consisted of lustrous crystals, m.p. 243° with decomposition.

Found %: I 36.83, 36.65. $C_{26}H_{30}S_2N_2I_2$. Calculated %: I 36.93.

Di-n-propiodide of α,ω-di-[4-phenylthiazolyl-(2)]-butane (V). 1.2 g of α,ω-di-[4-phenylthiazolyl-(2)]-butane (1 mole) was heated in a sealed tube on an oil bath at 140° for 12 hours with 1.3 g of n-propyl p-toluenesulfonate (2 moles). The yield was 0.25 g, or 34% of the theoretical. White crystals that turned yellow upon standing.

Di-n-butiodide of α,ω-di-[4-phenylthiazolyl-(2)]-butane (VI). 1.2 g of the base was heated with 1.4 g of n-butyl p-toluenesulfonate to 140° for 12 hours. The yield was 0.25 g, or 10% of the theoretical. Recrystallization from a 1:1 water-alcohol mixture yielded the di-n-butiodide as colorless crystals with a m.p. of 212°.

Found %: I 34.24. $C_{30}H_{38}N_2S_2I_2$. Calculated %: I 34.16.

DYES

3,3'-Diethyl-4,4'-dimethyl-6,8-dimethylenethiazolecarbocyanin p-toluenesulfonate (VII). 0.3 g of the di-(ethyl p-sulfonate) of α,ω-di-[4-methylthiazolyl-(2)]-butane was boiled for 20 minutes with 0.3 g of ethyl orthoformate and 2.5 ml of pyridine. The solution turned deep blue. We were unable to isolate the dye in the pure state, since it decomposed quickly. Its absorption maximum lay at 595 mμ.

3,3'-Diethyl-4,4'-diphenyl-6,8-dimethylenethiazolecarbocyanin p-toluenesulfonate (VIII). 1.5 g of the di-(ethyl p-sulfonate) of α,ω-di-[4-phenylthiazolyl-(2)]-butane was boiled with 1.5 g of ethyl orthoformate and 2 ml of pyridine for 20 minutes. The solution turned deep blue. The dye decomposed quickly. The absorption maximum lay at 596 mμ.

3,3'-Di-n-propyl-4,4'-diphenyl-6,8-dimethylenethiazolecarbocyanin p-toluenesulfonate (IX). 0.5 g of the di-(n-propyl p-toluenesulfonate) of α,ω-di-[4-phenylthiazolyl-(2)]-butane was boiled for 20 minutes with 0.5 g of ethyl orthoformate, and 2 ml of pyridine. A deep blue color appeared very quickly. The dye was unstable, and we were unable to secure it in the pure state. The absorption maximum lay at 600 mμ.

3,3'-Di-n-butyl-4,4'-diphenyl-6,8-dimethylenethiazolecarbocyanin p-toluenesulfonate (X). 0.1 g of the di-(n-butyl p-toluenesulfonate) of α,ω-di-[4-phenylthiazolyl-(2)]-butane and 0.1 g of ethyl orthoformate were boiled in 2 ml of pyridine to which 2-3 drops of acetic anhydride had been added. We were unable to isolate the dye in the pure state. Its absorption maximum lay at 600 mμ.

The author is deeply indebted to Prof. A. I. Kiprianov for his valuable counsel.

SUMMARY

1. Six new ditertiary salts have been synthesized by heating α,ω-di-[4-methylthiazolyl-(2)]-butane and α,ω-di-[4-phenylthiazolyl-(2)]-butane with dimethyl sulfate and the methyl, ethyl, n-propyl, and n-butyl esters of p-toluenesulfonic acid.

2. The dialkyl p-toluenesulfonates were condensed with ethyl orthoformate in pyridine or acetic anhydride; this yielded unstable α,γ-dimethylenethiazolecarbocyanins, which could not be recovered from their solutions. Their absorption maxima in ethyl alcohol have been determined.

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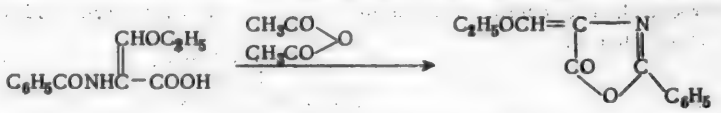
Institute of Organic Chemistry,
Ukrainian Academy of Sciences

THE REACTION OF THE DIETHYL ACETAL OF FORMYLHIPPURIC ACID WITH THIONYL CHLORIDE

A. S. Elina and O. Yu. Magidson

Study of complex molecules that contain diverse functional groups is of special interest, since it establishes the sensitivity of the individual functional groups to any reagent. The diethyl acetal of formylhippuric acid is a complex molecule of that type. We have investigated the reaction of the diethyl acetal of formylhippuric acid with thionyl chloride.

When the diethyl acetal of formylhippuric acid was reacted with thionyl chloride in a benzene solution (the benzene being absolutely anhydrous and the molar ratio being 1:1), we obtained a compound that contained no chlorine and might be taken to be ethoxymethylenehippuric acid, on the basis of its analysis. This was established by securing 2-phenyl-4-ethoxymethyleneoxazolinone-(5) when the substance was heated with acetic anhydride:



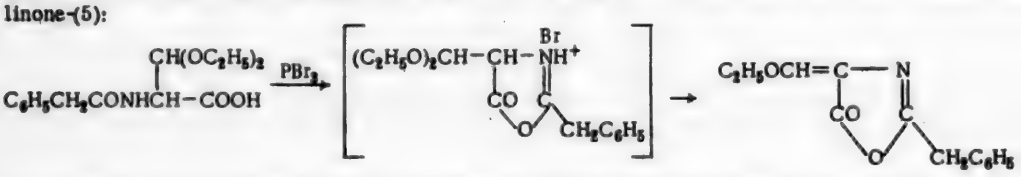
In contrast to the ethoxymethylene group in 2-phenyl-4-ethoxyoxazolinone-(5), the ethoxymethylene group in ethoxymethylenehippuric acid is highly alkali-resistant; it cannot be saponified, not only in the mild conditions employed to saponify the analogous group in 2-phenyl-4-ethoxymethyleneoxazolinone-(5), but not even when heated with an alkali.

Thus, the closure of the oxazolinone ring in this instance basically affects the reactivity of the ethoxymethylene group. In contrast to the ethyl ester of ethoxymethylenehippuric acid, which readily adds a molecule of alcohol in the presence of sodium ethoxide [1], producing the diethyl acetal of the formylhippurate, the ethoxymethylenehippuric acid does not add a molecule of alcohol under these conditions. When the proportions used in the reaction of the diethyl acetal of formylhippuric acid with thionyl chloride were 1:2.5, we obtained a crystalline compound that contained chlorine. This compound was very slightly soluble in benzene, chloroform, and carbon tetrachloride; it readily lost HCl, giving rise to 2-phenyl-4-ethoxymethyleneoxazolinone-(5), when it was heated in these solvents, when it was stored with the air excluded, and when it was treated with a $NaHCO_3$ solution or even with water. When a current of anhydrous HCl was passed through a chilled solution of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) in absolute benzene, we obtained its hydrochloride, whose crystalline form and properties were the same as those of the chlorine-containing compound we had secured by reacting 1 part of the diethylacetal of formylhippuric acid with 2.5 parts of thionyl chloride as described above. All these findings led us to conclude that when the diethyl acetal of formylhippuric acid is reacted with an excess of thionyl chloride(1:2.5), ethoxymethylenehippuric acid is first produced, after which the oxazolinone ring is closed and the hydrochloride of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) is formed. The closure of the oxazolinone ring may precede the stage in which the ethoxymethylenehippuryl chloride is formed; but if this compound exists, it is so unstable that it cannot be isolated. Our conclusions were further borne out by the fact that 2-phenyl-4-ethoxymethyleneoxazolinone-(5) was produced when equal parts of ethoxymethylenehippuric acid and thionyl chloride were reacted together. Moreover, when we interrupted the reaction of the diethyl acetal of formylhippuric acid with an excess of thionyl chloride (1:2.5 ratio) long before the crystalline hydrochloride of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) began to settle out of the benzene solution and then drove off the benzene in vacuo without applying any heat, we secured a nearly quantitative yield of 2-phenyl-4-ethoxymethyleneoxazolinone-(5).

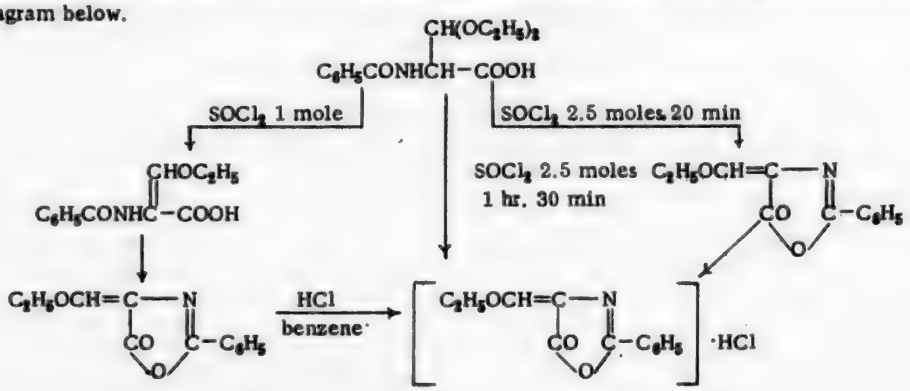
It is worthy of note that 2-phenyl-4-anilinomethyleneoxazolinone, whose m.p. was 164-165°, was produced by reacting the hydrochloride of 2-phenyl-4-ethoxymethyleneoxazolinone-(5), synthesized from the diethyl acetal of formylhippuric acid, with aniline, whereas the 2-phenyl-4-anilinomethyleneoxazolinone prepared from 2-phenyl-4-ethoxymethyleneoxazolinone-(5) had a m.p. of 154-155° after repeated recrystallization from alcohol, which is the melting point given in the literature [2]. The mixed melting point of these two anilinomethyleneoxazolinones

exhibited no depression. When the low-melting 2-phenyl-4-anilinomethyleneoxazolinone-(5) was recrystallized from alcohol to which a small quantity of the high-melting anilinomethyleneoxazolinone had been added, the low-melting anilinomethylene derivative was converted nearly quantitatively into the high-melting one with a m.p. of 164-165°.

The recently published monograph "The Chemistry of Penicillin" [3] states that the action of PBr_3 upon the diethyl acetal of α-formylphenaceturic acid yields the hydrobromide of 2-benzyl-4-ethoxymethyleneoxazolinone-(5). The authors believe the following to be the probable reaction mechanism involved: at first, the hydrobromide of 2-benzyl-4-diethoxymethyloxazolinone-(5) is formed, but it cannot be isolated because of its extreme instability, and it gives up a molecule of ethyl alcohol and is converted into the hydrobromide of 2-benzyl-4-ethoxymethyleneoxazolinone-(5):



We cannot accept this interpretation of the mechanism involved in this reaction, inasmuch as our researches (cited above) on a nearly analogous reaction, namely, the reaction of the diethyl acetal of formylhippuric acid with thionyl chloride, have shown that a molecule of ethyl alcohol is first split off, yielding ethoxymethylenehippuric acid, after which the ring is closed, forming 2-phenyl-4-ethoxymethyleneoxazolinone-(5), and finally, the latter's hydrochloride is produced. The reaction of the diethyl acetal of formylhippuric acid with thionyl chloride may be pictured by the diagram below.



EXPERIMENTAL

Ethoxymethylenehippuric acid. A solution of 0.85 g of the diethyl acetal of formylhippuric acid in 5.5 ml of absolute benzene was chilled while a solution of 0.37 g of $SOCl_2$ (1 mole per mole) in 3 ml of absolute benzene was slowly added. After the mixture had stood for 30-40 minutes at room temperature, the benzene was driven off in vacuo without the application of any heat. The residue, a brittle solid mass, was processed with a small amount of dichloroethane, the precipitated ethoxymethylenehippuric acid being filtered out. Another 0.1 g of ethoxymethylenehippuric acid was recovered from the mother liquor. Total yield was 0.5 g, or 70.4% of the theoretical.

After crystallization from dichloroethane the ethoxymethylenehippuric acid was a colorless crystalline substance with a m.p. of 187-188°, soluble when heated in water, but insoluble in ether.

7.599 mg substance: 0.392 ml N_2 (18°, 730.5 mm). 6.782 mg substance: 8.66 ml 0.02 N $Na_2S_2O_3$. Found %: N 5.82; OC_2H_5 19.17. $C_{12}H_{13}O_4N$. Calculated %: N 5.95; OC_2H_5 19.13.

Action of an alkali upon ethoxymethylenehippuric acid. a) A solution of 0.1 g of ethoxymethylenehippuric acid in 3 ml of 5% NaOH was allowed to stand for 4 hours at room temperature, after which it was acidulated until its reaction was acid with Congo red. A total of 0.09 g of the unchanged ethoxymethylenehippuric acid was recovered.

b) A solution of 0.1 g of ethoxymethylenehippuric acid in 4 ml of 5% NaOH was heated to 70-75° for 3 hours and then allowed to stand for 12 hours at room temperature. When the solution was acidulated, the ethoxymethylenehippuric acid was precipitated unchanged.

Action of absolute alcohol and sodium ethoxide upon ethoxymethylenehippuric acid. 0.27 g of ethoxymethylenehippuric acid was added to a solution of 0.03 g of Na in 5 ml of absolute alcohol, the solution was heated to

60-65° for two hours and set aside to stand at room temperature for 18 hours. The alcohol was driven off in vacuo, the residue dissolved in water, and the solution filtered and acidulated. The crystalline precipitate was filtered out, washed with water, and dried (0.24 g), m.p. 182-184°. The melting point of the substance rose to 188-189° after crystallization from water. The mixed melting point with ethoxymethylenehippuric acid exhibited no depression.

Synthesis of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) from ethoxymethylenehippuric acid. a) 0.3 g of ethoxymethylenehippuric acid was heated in 2 ml of acetic anhydride for 20 minutes on a water bath. The reaction solution was poured into water and processed with diethyl ether. The ether extract was treated a few times with a solution of $NaHCO_3$ and then with water, and dried with anhydrous Na_2SO_4, after which the ether was driven off. The residue, a crystalline substance (0.25 g), was recrystallized from petroleum ether. Recrystallization yielded a nearly colorless crystalline substance (needles) with a m.p. of 95-96°. The mixed melting point with 2-phenyl-4-ethoxymethyleneoxazolinone-(5) exhibited no depression.

b) 0.1 g of $SOCl_2$ in 2 ml of chloroform was gradually added to a chilled mixture of 0.21 g of ethoxymethylenehippuric acid and 7 ml of anhydrous chloroform. The ethoxymethylenehippuric acid slowly dissolved after the mixture had stood for 2 hours. The chloroform was driven off in vacuo at room temperature, leaving a residue of 0.19 g, which was dissolved in absolute benzene. The benzene was driven off until the residual volume was small, and petroleum ether was added as soon as crystals began to settle out. The precipitated crystalline substance was filtered out. Needles with a m.p. of 94-96°. The mixed melting point with 2-phenyl-4-ethoxymethyleneoxazolinone-(5) exhibited no depression.

Reaction of 1 mole of the diethyl acetal of formylhippuric acid with 2.5 moles of thionyl chloride. a) 1.1 g of $SOCl_2$ in 2 ml of absolute benzene was gradually added to a chilled solution of 1 g of the diethyl acetal of formylhippuric acid in 6 ml of absolute benzene. After the mixture had stood for 20 minutes at room temperature, the benzene was driven off in vacuo without the application of any heat. The residue was crystallized from petroleum ether, yielding a crystalline substance with a m.p. of 93-95°, which possessed all the properties of 2-phenyl-4-ethoxymethyleneoxazolinone-(5). Recrystallization from petroleum ether yielded nearly colorless needles with a m.p. of 95-96°, whose mixed melting point with 2-phenyl-4-ethoxymethyleneoxazolinone-(5) exhibited no depression.

b) 1.1 g of $SOCl_2$ in 2 ml of absolute benzene was gradually added to a chilled solution of 1 g of the diethyl acetal of formylhippuric acid in 6 ml of absolute benzene. After the mixture had stood for 1.5 hours at room temperature, the nearly colorless crystalline precipitate of the hydrochloride of 2-phenyl-4-ethoxymethyleneoxazolinone-(5), weighing 0.6 g, was filtered out. It was thoroughly washed free of the reaction solution by repeatedly mixing it with absolute benzene, filtering it out, and rewashing it on the filter.* 2-Phenyl-4-ethoxymethyleneoxazolinone-(5) hydrochloride is insoluble in ether, benzene, dichloroethane, chloroform, or carbon tetrachloride; it decomposes upon standing, giving off HCl and yielding 2-phenyl-4-ethoxymethyleneoxazolinone-(5). A quantitative yield of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) was produced when the 2-phenyl-4-ethoxymethyleneoxazolinone-(5) was treated with a $NaHCO_3$ solution or with water. 2-Phenyl-4-ethoxymethyleneoxazolinone-(5) hydrochloride does not have a sharp melting point, fusing between 90 and 94°. The 2-phenyl-4-ethoxymethyleneoxazolinone-(5) hydrochloride apparently breaks down in the capillary, yielding 2-phenyl-4-ethoxymethyleneoxazolinone-(5).

8.394 mg substance: 4.415 mg AgCl. Found %: Cl 13.01. $C_{12}H_{11}O_3N \cdot HCl$. Calculated %: Cl 13.98.

2-Phenyl-4-ethoxymethyleneoxazolinone-(5) hydrochloride from 2-phenyl-4-ethoxymethyleneoxazolinone-(5). A current of dry HCl was passed through a chilled solution of 1.5 g of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) in 15 ml of absolute benzene for 5 minutes. Crystals of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) hydrochloride begin to settle out as soon as the passage of the HCl is initiated. The 2-phenyl-4-ethoxymethyleneoxazolinone-(5) hydrochloride was filtered out and processed repeatedly with absolute benzene, after which it was a nearly colorless crystalline substance that was insoluble in ether, benzene, chloroform, dichloroethane, or carbon tetrachloride. All the other properties of this substance were the same as those of the 2-phenyl-4-ethoxymethyleneoxazolinone hydrochloride prepared from the diethyl acetal of formylhippuric acid, m.p. 90-94°.

High-melting 2-phenyl-4-anilinomethyleneoxazolinone-(5). 0.15 g of aniline was added to 0.2 g of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) in 2 ml of absolute $CHCl_3$. The initial substance dissolved gradually, a colorless crystalline precipitate – aniline hydrochloride – being thrown down. The aniline hydrochloride (0.1 g) was filtered out. The solution was evaporated, and the 0.8 g of yellow crystalline precipitate was crystallized a few times from ethyl alcohol. 2-Phenyl-4-anilinomethyleneoxazolinone-(5) consisted of yellow needles with a m.p. of 164-165°.

5.564 mg substance: 0.519 ml N_2 (20.5° at 743 mm). Found %: N 10.6. $C_{16}H_{12}O_2N_2$. Calc.%: N 10.61.

*0.2 g of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) was recovered from the benzene mother liquor after the benzene had been driven off.

2-Phenyl-4-anilinomethyleneoxazolinone-(5) from 2-phenyl-4-ethoxymethyleneoxazolinone-(5). 0.33 g of aniline was added to a solution of 0.35 g of 2-phenyl-4-ethoxymethyleneoxazolinone-(5) in 3 ml of ethyl alcohol. A yellow crystalline precipitate began to settle out at once; after the mixture had stood for a few minutes, the precipitate (0.41 g) was filtered out and crystallized from ethyl alcohol. The m.p. of 2-phenyl-4-anilinomethyleneoxazolinone-(5) (yellow needles) was 154-155° after four crystallizations from ethyl alcohol. The mixed melting point with the high-melting 2-phenyl-4-anilinomethyleneoxazolinone-(5) was 164-165°.

The 2-phenyl-4-anilinomethyleneoxazolinone-(5) with a m.p. of 154-155° was recrystallized from ethyl alcohol to which a small amount of the high-melting 2-phenyl-4-anilinomethyleneoxazolinone-(5) had been added. The anilinomethylene derivative secured after this crystallization had a m.p. of 164-165°.

SUMMARY

1. It has been found that when equal molar proportions of the diethyl acetal of formylhippuric acid and thionyl chloride are reacted together, a molecule of ethyl alcohol is split out and ethoxymethylenehippuric acid is formed, which reacts with acetic anhydride or thionyl chloride (1 mole: 1 mole) to yield 2-phenyl-4-ethoxymethyleneoxazolinone-(5).

2. It has been proved that the ethoxymethylene group in ethoxymethylenehippuric acid differs from the analogous group in 2-phenyl-4-ethoxymethyleneoxazolinone-(5) in resisting the action of an alkali.

3. It has been established that when 1 mole of the diethyl acetal of formylhippuric acid is reacted with 2.5 moles of thionyl chloride, 2-phenyl-4-ethoxymethyleneoxazolinone-(5) is formed, while prolonged interaction yields the hydrochloride of 2-phenyl-4-ethoxymethyleneoxazolinone-(5).

4. The reaction mechanism proposed by the American authors Hunter, Hinman, and Carter for the formation of salts of 2-phenyl-4-alkoxymethyleneoxazolinones is utterly unfounded.

5. It has been established that 2-phenyl-4-anilinomethyleneoxazolinone-(5) exists in two forms: the low-melting (154-155°) and the high-melting (164-165°), and the conversion of the low-melting form into the high-melting one has been effected.

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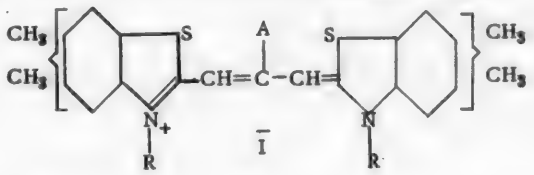
Laboratory of Heterocyclic Compounds,
The S. Ordzhonikidze All-Union Research Institute
of Pharmaceutical Chemistry

RESEARCHES ON CYANIN DYES

VII. THE PROPERTIES OF TETRAMETHYLTHIACARBOCYANINS

I.I.Levkoev, A.F.Vompe, N.N.Sveshnikov, and N.S.Barvin

In several symmetrical thiacarbocyanins, the entrance of electron donor groups at the 5,5' and 6,6' positions shifts the absorption maximum of the dyes appreciably toward the longer wavelengths, whereas the presence of the same groups at the 4,4' or 7,7' position deepens the color of the dye only slightly [1-6]. We were interested in ascertaining the effect of the entrance of two identical or dissimilar electron donor groups at different positions in the heterocyclic rings upon the optical and photographic properties of the thiacarbocyanins. It was advisable to begin with a study of the symmetrical dyes of this class, which contain 4 identical substituent groups in various positions on the heterocyclic rings. In the present research, we have synthesized and investigated several 4,5,4',5'-, 4,6,4',6'-, 4,7,4',7'-, 5,6,5',6'-, 5,7,5'7'- and 6,7,6',7'-tetramethylthiacarbocyanins (I).



A = H or CH_3 ($R = C_2H_5$) or
A = C_2H_5 ($R = CH_3$ or C_2H_5)

(I)

Of all these dyes, only a few 5,6,5',6',-derivatives are cited in one of the patents [7], being suggested as sensitizers for silver halide emulsions. According to this patent, the entrance of methyl groups at the 5,6,5',6', positions in thiacarbocyanins produces a fairly substantial bathochromic shift of the absorption maximum.

We synthesized the initial 2,4,5-, 2,4,7- and 2,5,7-trimethylbenzothiazoles, as well as the 2,4,6-trimethylbenzothiazole described previously [8], by oxidizing the thioacetyl derivatives of the respective aminoxylenes with potassium ferricyanide (see [9]). The 2,5,6- and 2,6,7-trimethylbenzothiazoles were synthesized by heating the respective 2-aminodimethylbenzothiazoles with potassium hydroxide and processing the resulting salts of aminothioxylenes with acetic anhydride [10].

TABLE 1

Location of the Absorption Maxima of the Ethylates of Di- and Tetramethylcarbocyanins (In Ethyl Alcohol)

Location of methyl groups	Location of absorption maxima (in mμ)		
	Substituents at the 9 position		
	H	CH_3	C_2H_5
–	557	543	547
4,4'-[1]*	563	547	–
5,5'-	565	548	550
6,6'-	563	548	552
4,5,4',5'-	568	550	553
4,6,4',6'-	568	552	556
4,7,4',7'-	566	550	554
5,6,5',6'-	570	554	558
5,7,5',7'-	568	553	557
6,7,6',7'-	568	553	557

Most of the dyes were synthesized by heating the reactive alkyl p-toluenesulfonates of the isomeric trimethylbenzothiazoles with ortho esters of carboxylic acids in pyridine [11] and were isolated as well-crystallized iodides. Inasmuch as the yields of the alkyl p-toluenesulfonates of the 2,4,5-trimethylbenzothiazoles are low when produced under ordinary conditions, we employed the respective alkylalkyl sulfates, previously isolated in the pure state, in synthesizing the dyes.

The absorption maxima of the ethylates of the synthesized tetramethylthiacarbocyanins and of some dimethyl derivatives are listed in Table 1.

We see from the table that the color is deepened whenever a dimethylthiacarbocyanin is converted into a tetramethylthiacarbocyanin. The

* Footnote [1] refers to the 4,4-dimethylthiacarbocyanins, since the cited values of the absorption maxima for these dyes were taken from the paper cited.

5,6,5',6'-tetramethyl derivative exhibits the greatest shift of the absorption maximum toward the longer wavelengths, as compared to the unsubstituted dye, while the least deepening of color is exhibited by the 4,7,4',7' substitution derivative of the dye. Hence, the second substituent group produces a greater shift of the absorption maximum toward the longer wave-lengths in tetramethylthiacarbocyanins when it enters at the 5,5' and 6,6' positions.

The tetramethylthiacarbocyanins are sensitizers of average efficiency. The ability of the corresponding 9-alkyl derivatives to act as second-order sensitizers is rather slight, being somewhat greater in the 5,6,5',6' substitution derivatives.

EXPERIMENTAL

(Together with A. G. Guseva and N. S. Stokovskaya)

Synthesis of Intermediates

3-Thioacetamino-1,2-xylene. 3.35 g of pulverized phosphorus pentasulfide was gradually added to a boiling solution of 8.15 g of 3-acetamino-1,2-xylene with a m.p. of 134-135° [12] in 35 ml of anhydrous benzene, and the mixture was then boiled for 30 minutes. The benzene solution was decanted from the tarry mass, which was washed with 75 ml of benzene. The benzene solutions were combined and then agitated with a 4% sodium hydroxide solution (three times, using 50-ml portions). The alkaline solution was neutralized with acetic acid and by passing carbon dioxide through. The 3-thioacetamino-1,2-xylene was recovered as a colorless crystalline precipitate. The yield was 5.0 g (62.5% of the theoretical). M.p. 130-131°.

Colorless prisms with a m.p. of 134-135°, after 3 recrystallizations from 50% ethyl alcohol.

Found %: N 7.75. $C_{10}H_{13}NS$. Calculated %: N 7.82.

4-Thioacetamino-1,3-xylene. This was produced like the preceding compound, by boiling a solution of 10 g of 4-acetamino-1,3-xylene, with a m.p. of 127° [13], in 60 ml of benzene for one hour with 4.08 g of phosphorus pentasulfide. The yield was 60% of the theoretical. M.p. 68°.

Crystallization from 50% ethyl alcohol yielded colorless crystals with a m.p. of 93° (Jacobson and Ney [8] give the m.p. as 94-95°).

5-Thioacetamino-1,3-xylene. A mixture of 4.37 g of 5-acetoamino-1,3-xylene, with a m.p. of 142° (Wroblewsky [14] gives the m.p. of 144.33°, while Noelting and Forel [12] give it as 140.5°), and 1.78 g of phosphorus pentachloride was added to 30 ml of boiling anhydrous benzene during the course of 1 hour, after which the liquid was refluxed for 2 hours. The product was isolated in the same way as was the 3-thioacetamino-1,3-xylene. The yield was 2.87 g (59.8% of the theoretical). M.p. 91-92°. Nearly colorless crystals with a m.p. of 93° (from ethyl alcohol).

Found %: N 7.95, 7.67. $C_{10}H_{13}NS$. Calculated %: N 7.82.

2-Thioacetamino-1,4-xylene. This was prepared, like the preceding compound, by reacting 5.4 g of 2-acetamino-1,4-xylene, with a m.p. of 137-138° (Schaumann [15] gives the m.p. as 138-139°, while Noelting, Witt, and Forel [16] give 139°), with 2.2 g of phosphorus pentasulfide in 35 ml of boiling benzene. The yield was 56.5% of the theoretical. Colorless crystals (from ethyl alcohol), m.p. 76°.

Found %: N 7.81. $C_{10}H_{13}NS$. Calculated %: N 7.82.

2,4,5-Trimethylbenzothiazole. A solution of 3.58 g of 3-thioacetamino-1,2-xylene (with a m.p. of 130-131°) in 80 ml of 4% potassium hydroxide was gradually added, with vigorous stirring, at 3-5° to a solution of 13.2 g of potassium ferricyanide in 55 ml of water. The mixture was stirred for 2 hours, after which the precipitate was extracted with ether, the ether driven off, and the residue distilled with steam. The distillate was extracted with ether, the extract dried with potash, and the ether driven off, the residue turning into a colorless crystalline mass when chilled. The yield was 2.80 g (79% of the theoretical). M.p. 50-51°.

The base was secured as colorless prisms with a m.p. of 54-55° after distillation in vacuo (b.p. 149-150° at 19 mm) and triple crystallization from gasoline.

Found %: N 7.78. $C_{10}H_{11}NS$. Calculated %: N 7.91.

Picrate. Large yellow prisms (from ethyl alcohol). M.p. 142-143°.

Found %: N 13.68. $C_{16}H_{14}O_7N_6S$. Calculated %: N 13.79.

Methylmethyl sulfate. This was prepared by heating 1.06 g of 2,4,5-trimethylbenzothiazole with 0.78 g of

dimethyl sulfate on a boiling water bath for 3 hours. The crystallized mass was washed with ether and acetone. The yield was 1.55 g (83% of the theoretical).

Minute colorless prisms (from acetone), m.p. 213-215° (with decomposition).

Found %: N 4.60. $C_{12}H_{17}O_4NS_2$. Calculated %: N 4.61.

Methiodide. An 81.2% yield of this derivative was secured by adding potassium iodide to an aqueous solution of the preceding compound.

Colorless prisms (from ethyl alcohol), m.p. 215-216°.

Found %: N 4.42. $C_{11}H_{14}NSI$. Calculated %: N 4.38.

Ethylethyl sulfate. A mixture of 1.06 g of 2,4,5-trimethylbenzothiazole and 0.87 g of diethyl sulfate was heated to 130° for 5 hours. The crystalline mass was washed with anhydrous ether and triturated with 3 ml of anhydrous acetone. The precipitate was filtered out and washed with 2 ml of acetone. The yield was 0.35 g. M.p. 208-209°. Colorless prisms (from acetone), m.p. 215-217°. Very freely soluble in ethyl alcohol and in water.

Found %: N 4.32. $C_{14}H_{21}O_4NS_2$. Calculated %: N 4.20.

The acetone mother liquor and the wash liquid, which contained the ethyl sulfate salt of the base, were evaporated to dryness, the residue being dissolved in 10 ml of water, and 0.5 g of pyridine added to it.

The resultant bases were extracted with ether, and the aqueous solution was evaporated until its volume totaled 3 ml, after which 0.5 g of potassium iodide was added to it. The precipitated 2,4,5-trimethylbenzothiazole methiodide was filtered out and washed with water and acetone. The yield was 0.18 g. M.p. 204-205°.

0.35 g of 2,4,5-trimethylbenzothiazole, with a m.p. of 51-52°, was recovered from the ether solution of the wash water of the ethylethyl sulfate reaction. Another 0.20 g of the base was isolated from the ether solution produced by decomposing the ethyl sulfate salt with pyridine. The total yield of the quaternary salt was 26% of the theoretical, or 55% on the basis of the reacted base.

Ethiodide. Slightly grayish needles (from ethyl alcohol). M.p. 205-206°.

Found %: N 4.33. $C_{12}H_{16}NSI$. Calculated %: N 4.20.

2,4,6-Trimethylbenzothiazole. This was synthesized, like the preceding base, by adding 5.37 g of 4-thioacetamino-1,3-xylene in 120 mo of 4% sodium hydroxide to a solution of 20.6 g of potassium ferricyanide in 80 ml of water. The next day the liquid was extracted with ether, the extract dried with potash, the ether driven off, and the residue distilled in vacuo. A fraction with a b.p. of 146-148° at 15 mm was collected. The yield was 56.5% of the theoretical (when Jacobson and Nay [8] synthesized 2,4,6-trimethylbenzothiazole, their yield was 32%). Slightly yellowish oil.

Picrate. Yellow prisms with a m.p. of 138-139° (after double recrystallization from ethyl alcohol).

2,4,7-Trimethylbenzothiazole. This was synthesized, like the preceding base, by oxidizing 2-thioacetamino-1,4-xylene with potassium ferricyanide. The residue crystallized completely after the ether had been driven off. The yield was 97% of the theoretical. M.p. 29°. The base was purified by distilling it in vacuo. B.p. 132-133° at 9 mm. Colorless acicular crystals, m.p. 29°.

Found %: N 7.95. $C_{10}H_{11}NS$. Calculated %: N 7.91.

Picrate. Large light-yellow prisms (from ethyl alcohol). M.p. 142°.

Found %: N 13.90, 13.84. $C_{16}H_{14}O_7N_4S$. Calculated %: N 13.79.

2,5,7-Trimethylbenzothiazole. A filtered solution of 2.52 g of 5-thioacetamino-1,3-xylene in 60 ml of 4% potassium hydroxide was gradually added, with vigorous stirring, during the course of one hour to a solution of 9.65 g of potassium ferricyanide in 35 ml of water, chilled to 3-5°. A gray crystalline precipitate was thrown down. After two hours of stirring, the precipitate was filtered out, washed with water, and dried. The yield was 2.3 g (92% of the theoretical). M.p. 79-80°. The base was purified by crystallizing it twice from gasoline. Colorless prisms with a m.p. of 84°.

Found %: N 7.99, 8.02. $C_{10}H_{11}NS$. Calculated %: N 7.91.

Picrate. Yellow needles (from ethyl alcohol). M.p. 176°.

TABLE 2

Name of dye	Base, g	p-Toluene-sulfonate, g	Ortho ester and its quantity, g	Ml of pyri-dine	% of theoretical yield
3,3'-Diethyl-4,6,4',6'-tetramethylthiacarbocyanin iodide	0.18	0.22	I—0.30	1.0	29
3,3'-Diethyl-4,6,4',6',9'-pentamethylthiacarbocyanin iodide	0.53	0.66	II—1.46*	3.0	22
3,3'9-Triethyl-4,6,4',6'-tetramethylthiacarbocyanin iodide	0.53	0.66	III—0.79**	3.0	14
3,4,6,3',4',6'-Hexamethyl-9-ethylthiacarbocyanin iodide	0.18	0.20	III—0.26	1.0	22
3,3'-Diethyl-4,7,4',7'-tetramethylthiacarbocyanin iodide	0.18	0.22	I—0.30	1.0	26
3,3'-Diethyl-4,7,4',7',9-pentamethylthiacarbocyanin iodide	0.53	0.66	II—1.46*	3.0	15
3,3',9-Triethyl-4,7,4',7' -tetramethylthiacarbocyanin iodide	0.53	0.66	III—0.79**	3.0	13
3,3'-Diethyl-5,6,5',6'-tetramethylthiacarbocyanin iodide	0.18	0.22	I—0.30	1.0	95
3,3'-Diethyl-5,6,5',6',9-pentamethylthiacarbocyanin iodide	0.53	0.66	II—0.97	3.0	53.5
3,3',9-Triethyl-5,6,5',6'-tetramethylthiacarbocyanin iodide	0.53	0.66	III—0.79	2.0	63
3,5,6,3',5',6'-Hexamethyl-9-ethylthiacarbocyanin iodide	0.71	0.82	III—1.06	4.0	63
3,3'-Diethyl-5,7,5',7',-tetramethylthiacarbocyanin iodide	0.18	0.22	I—0.30	1.0	55
3,3'-Diethyl-5,7,5',7',9-pentamethylthiacarbocyanin iodide	0.53	0.66	II—1.46	3.0	23
3,3',9-Triethyl-5,7,5',7'-tetramethylthiacarbocyanin iodide	0.53	9.66	III—0.79	3.0	12
3,5,7,3',5',7'-Hexamethyl-9-ethylthiacarbocyanin iodide	0.18	0.22	III—0.26	1.0	55
3,3'-Diethyl-6,7,6',7'-tetramethylthiacarbocyanin iodide	0.18	0.22	I—0.30	1.0	65
3,3'-Diethyl-6,7,6',7',9-pentamethylthiacarbocyanin iodide	0.18	0.22	II—0.32	1.0	53
3,3',9-Triethyl-6,7,6',7'-tetramethylthiacarbocyanin iodide	0.18	0.22	III—0.26	1.0	45
3,6,7,3',6',7'-Hexamethyl-9-ethylthiacarbocyanin	0.18	0.20	III—0.26	1.0	44

NOTES. I. Ethyl orthoformate. II. Ethyl orthoacetate. III. Ethyl orthopropionate.

* 0.15 gram of acetic anhydride added.

** 0.19 gram of propionic anhydride added.

Found %: N 13.60. $C_{16}H_{14}O_7N_4S$. Calculated %: N 13.79.

Dyes

3,3'-Diethyl-4,5,4',5'-tetramethylthiacarbocyanin iodide. A mixture of 0.16 g of ethylethyl sulfate of 2,4,5-trimethylbenzothiazole, 0.15 g of ethyl orthoformate, and 0.5 ml of pyridine was heated for an hour on an oil bath at 130-135°. Ether was added to the solution, the tarry precipitate being dissolved in ethyl alcohol, and the dye being recovered by adding an equal volume of a 10% solution of potassium iodide. The yield was 0.10 g (71% of the theoretical). M.p. 240-241°. Dull grayish-blue needles with a m.p. of 243-245° after crystallization from ethyl alcohol.

Found %: N 5.23. $C_{25}H_{29}N_2S_2I$. Calculated %: N 5.11.

3,3'-Diethyl-4,5,4',5',9'-pentamethylthiacarbocyanin iodide. This was synthesized, like the preceding dye, from ethyl orthoformate (0.16 g). The yield was 57% of the theoretical. Dark-green needles (from ethyl alcohol), m.p. 222-223°.

Found %: N 4.86. $C_{26}H_{31}N_2S_2I$. Calculated %: N 4.98.

3,3',9-Triethyl-4,5,4',5'-tetramethylthiacarbocyanin iodide. This was synthesized, like the dye without a chain substituent, by condensing 0.35 g of 2,4,5-trimethylbenzothiazole ethylethyl sulfate with 0.26 g of ethyl

TABLE 2 (continued)

Appearance	M.p.(with decomposition)	Absorption maximum (in mμ)	% N found	Calculated	
				Formula	% N
Lustrous dark-green needles	248°	568	5.08	$C_{25}H_{29}N_2S_2I$	5.11
Thin dark-violet needles	234	552	5.16	$C_{26}H_{31}N_2S_2I$	4.98
Minute dark-green prisms	229	556	4.86	$C_{27}H_{33}N_2S_2I$	4.86
Brownish-red prisms	206	551	5.16	$C_{25}H_{29}N_2S_2I$	5.11
Dark-green needles with a golden sheen	262	566	5.26	$C_{25}H_{29}N_2S_2I$	5.11
Blue-violet prisms	223	550	5.17	$C_{26}H_{31}N_2S_2I$	4.98
Brown prisms with a green tinge	208	554	5.01	$C_{27}H_{33}N_2S_2I$	4.86
Dark-green prisms with a golden sheen	260	570	4.97	$C_{25}H_{29}N_2S_2I$	5.11
Red-violet needles	275	554	4.84	$C_{26}H_{31}N_2S_2I$	4.98
Dark-blue needles	248-249	558	4.66	$C_{27}H_{33}N_2S_2I$	4.86
Red-violet prisms	253	554	4.96	$C_{25}H_{29}N_2S_2I$	5.11
Red-brown prisms with a greenish sheen	275	568	5.19	$C_{25}H_{29}N_2S_2I$	5.11
Grayish-blue needles	271	553	5.03	$C_{26}H_{31}N_2S_2I$	4.98
Green prisms	255	557	4.84	$C_{27}H_{33}N_2S_2I$	4.86
Brownish-red prisms	257	554	5.07	$C_{25}H_{29}N_2S_2I$	5.11
Green prisms with a golden sheen	287-288	568	5.06	$C_{25}H_{29}N_2S_2I$	5.11
Grayish-blue prisms	272-273	553	5.12	$C_{26}H_{31}N_2S_2I$	4.98
Dark-green prisms with a golden sheen	242-243	557	4.70	$C_{27}H_{33}N_2S_2I$	4.86
Minute dark-red prisms	253-254	555	5.26	$C_{25}H_{29}N_2S_2I$	5.11

orthoformate in 2 ml of pyridine. After the dye had been precipitated with ether, it was converted into the iodide in alcohol solution. The yield was 41.4% of the theoretical. Dark-green prisms with a golden sheen (from ethyl alcohol). M.p. 218-220°.

Found %: N 5.01. $C_{27}H_{33}N_2S_2I$. Calculated %: N 4.86.

3,4,5,3',4',5'-Hexamethyl-9-ethylthiacarbocyanin iodide. This was synthesized by heating 0.3 g of 2,4,5-trimethylbenzothiazole methylmethyl sulfate with 0.26 g of ethyl orthoformate, 1 ml of pyridine, and 0.05 g of acetic anhydride to 130° for 1 hour. The dye was precipitated with ether and converted into the iodide in the usual manner. The yield was 44.4% of the theoretical. The preparation was purified by double recrystallization from ethyl alcohol. Red-brown prisms with a m.p. of 210-211°. Absorption maximum at 550 mμ.

Found %: N 5.03. $C_{25}H_{27}N_2S_2I$. Calculated %: N 5.11.

4,6,4',6'-, 4,7,4',7'-, 5,6,5',6'-, 5,7,5',7'- and 6,7,6',7'-Tetramethylthiacarbocyanins. The 3,3'-diethyl-tetramethylthiacarbocyanins were synthesized by refluxing the respective trimethylbenzothiazoles with a 10% excess of ethyl p-toluenesulfonate for 6 hours on an oil bath at 140-150°. The quaternary salts of the 3,3'-diethyl derivatives were synthesized at 130-135°. Anhydrous pyridine and the ortho ester of the carboxylic acid were added to the quaternary salt (sometimes acetic or propionic anhydride was used), and the mixture was heated to 130-135° for 1 hour. The cooled reaction solution was diluted with ether, the precipitate or tarry mass thrown down being dissolved by boiling in ethyl alcohol, and the dye being recovered by adding an equal volume of a 10% solution of potassium iodide.

The dye was purified by crystallizing it from ethyl alcohol until its melting point remained constant; it was dried at 50-60° in vacuo over phosphoric anhydride before being analyzed. The dyes' synthesis conditions, properties, and analysis results are given in Table 2.

The absorption curves of the dyes were plotted in a $1 \cdot 10^{-4}$ molar solution in ethyl alcohol, using a Koenig-Martens spectrophotometer.

SUMMARY

1. Twenty–three symmetrical tetramethylthiacarbocyanins have been synthesized, containing methyl groups at various positions in the benzene rings of the heterocyclic residues. 2,4,5-, 2,4,7, and 2,5,7-trimethylbenzothiazoles have been synthesized, plus some derivatives of these bases.

2. It has been shown that the transition from dimethyl- to tetramethylthiacarbocyanins always involves a shift of the dye's absorption maximum toward the longer wave-lengths of the spectrum, the entrance of the methyl groups at the 5,5' and 6,6' positions producing a greater bathochromic shift.

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All-Union Institute of Cinema and Photographic Research

THE EFFECT OF ACTIVATED CHARCOAL UPON THE OXIDATION OF PAPAVERINE BY ATMOSPHERIC OXYGEN

A.S.Labensky

One of the tests of the quality of pharmacopeial papaverine hydrochloride is its reaction with concentrated sulfuric acid. The Pharmacopeia of the USSR (8th ed.), like the pharmacopeias of several other countries, requires that papaverine hydrochloride dissolve in concentrated sulfuric acid without producing any coloration. A product that is not pure enough usually turns the solution violet.

In his time, Merck [1], who discovered papaverine, thought that the appearance of this coloration was a characteristic property of papaverine. Hesse [2] subsequently recrystallized papaverine acid oxalate and secured a product that did not cause any coloration when tested with concentrated sulfuric acid. Hesse thus showed that the appearance of a coloration when papaverine was dissolved in sulfuric acid had to be attributed to some unknown impurity in the papaverine. The same author [3] worked on the problem of isolating this impurity from commercial papaverine; he reported that he had isolated a new substance, which he called papaveramine. This substance produced a strong violet coloration when dissolved in concentrated sulfuric acid. Somewhat later Pictet and Kramer [4] also worked on the problem of isolating from commercial papaverine the impurity whose presence in the papaverine produces the violet coloration during the test with concentrated sulfuric acid. These researchers found no papaveramine, though they did isolate a substance that produced a violet coloration when dissolved in sulfuric acid. This substance proved to be the alkaloid cryptopine.

Ever since, it has been established doctrine in scientific circles that the violet coloration that appears when papaverine is tested with sulfuric acid is due to the presence of cryptopine. However, as our own researches have indicated, the problem of the appearance of the violet coloration when papaverine is dissolved in sulfuric acid must be explained otherwise. The present research was undertaken to shed light upon this cause.

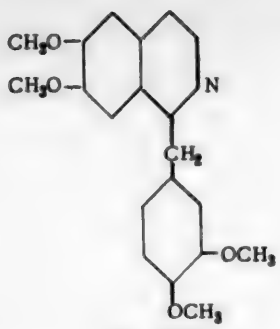
In the course of a long study of the problem of refining the papaverine secured from opium into a pharmacological product we discovered one interesting fact. We noticed that even absolute papaverine, which causes no coloration when dissolved in sulfuric acid, can be converted under certain conditions into a product that does produce this coloration. Upon a more detailed investigation of this phenomenon we found that this transformation of papaverine takes place in the following instances. First, this transformation occurs most readily when activated charcoal is used to refine aqueous solutions of papaverine. Second, a similar change in the papaverine, though not so pronounced occurs when the base papaverine is recovered from hot aqueous solutions of its salts by ammonia or other alkalies.

These indicate beyond the shadow of a doubt that the reason for the appearance of a violet color when papaverine is tested with sulfuric acid is the presence of some product of a transformation of the papaverine itself.

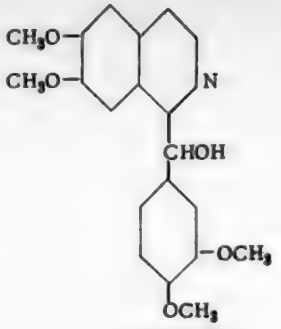
It is most likely that this product is a product of the oxidation of papaverine.

We know from the literature that the substance that is an oxidation product of papaverine and is also able to bring about a violet coloration when dissolved in concentrated sulfuric acid is papaverinol.

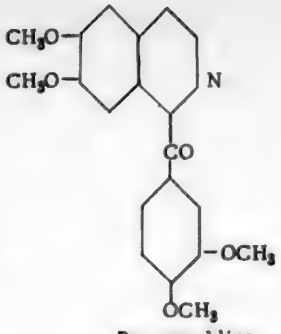
Stuchlik [5] synthesized papaverinol by reducing papaveraldine—a product first obtained by Goldschmidt [6] by oxidizing papaverine. Papaverinol is thus a product of the intermediate oxidation of papaverine to papaveraldine, as may be seen from their structural formulas:



Papaverine



Papaverinol



Papaveraldine

Inasmuch as the structural formula for papaverine contains a readily oxidizable methylene group located between two rings, it is highly probable that during the refining of papaverine the latter may be partially oxidized to papaverinol. The presence of the latter as an impurity in the papaverine would bring about the violet coloration when the papaverine is tested with sulfuric acid. It would be desirable, however, to produce experimental proof that this is so.

As we stated above, the most striking change in papaverine (in so far as its behavior in the sulfuric acid test is concerned) takes place when aqueous solutions of its salts are treated with activated charcoal. We therefore resolved to make use of this phenomenon in setting up our experiment.

We did this by adding enough activated charcoal to a solution of pure papaverine hydrochloride to have nearly all the alkaloids absorbed by the charcoal after air had been blown through the heated solution. Then the alkaloids were desorbed by chloroform. Two oxidation products of papaverine, papaveraldine and papaverinol, were found in the resulting chloroform solution.

This experiment proved that papaverine could be oxidized by atmospheric oxygen in the presence of activated charcoal yielding papaverinol, a substance that produces a violet coloration when it is dissolved in sulfuric acid.

We think the following fact should also be cited by way of supplementary proof: papaverine produced synthetically, in which no cryptopine or any other opium alkaloid can be present, almost always produces a violet coloration when tested with sulfuric acid (unless it is specially purified).

With papaverinol at our disposal, we were greatly interested in determining the sensitivity of the reaction of this substance with sulfuric acid that produces a violet coloration. We found that this is an extremely sensitive reaction, viz.: the coloration is still perceptible at a dilution of 1:1,000,000, whereas the color is nearly imperceptible in a layer 16 mm thick (diameter of the test tube) at a dilution of 1:2,000,000. The test temperature was +23°.

Once we know the sensitivity of this reaction, we can calculate that a 0.025% trace of papaverinol in the papaverine suffices to produce a violet coloration when papaverine is tested with sulfuric acid as prescribed by the pharmacopeia.

EXPERIMENTAL

6 grams of pure papaverine hydrochloride was dissolved in 250 ml of water, and 20 g of activated charcoal (O.U. brand) was added to the solution. A current of air was then passed through the solution at 70° for 15 hours. The charcoal was filtered out, and a dark amorphous precipitate weighing 0.3 g was thrown down from the solution by adding ammonia until the reaction was alkaline. The bulk of the alkaloid was obviously adsorbed by the activated charcoal.

The activated charcoal was triply extracted with chloroform, using 150 ml in each extraction. After the chloroform had been driven off, the residue consisted of a dark crystalline mass weighing 3.6 g. The residue was dissolved in 100 ml of 10% sulfuric acid. The small amount of undissolved residue was filtered out. Then the solution was diluted with twice its volume of water and agitated three times with chloroform, using 80 ml of the latter each time. The acid solution was then alkalinized with ammonia until the odor of the latter was clearly perceptible, and the alkaline solution was again agitated with chloroform 3 times, using 80 ml each time. The chloroform extracts, secured from the acid as well as from the alkaline solutions, were dried separately with calcined sodium sulfate. Driving off the chloroform from the extract obtained by extracting the acid aqueous solution yielded 2 g of

a crystalline residue. Driving off the solvent from the extract obtained by extracting the alkaline solution yielded 1.3 g of a dark amorphous mass.

The first residue was dissolved by heating it in 50 ml of a 5% hydrochloric acid solution. The solution was filtered while hot. As it cooled, crystals settled out as minute elongated yellow needles. The 2.2 g of yellow crystals was recrystallized from 50 ml of 5% hydrochloric acid. The new crystalline precipitate was dissolved by heating it in 15 ml of ethyl alcohol. When aqueous ammonia was added to this alcoholic solution, a fine, white, crystalline precipitate was rapidly thrown down. The precipitate weighed 1.2 g, m.p. 209-210°. Its mixed melting point with the papaveraldine we had synthesized from papaverine by the Pschorr method [7], as modified by Kabachnik and Zitser [8], exhibited no depression.

The second, amorphous precipitate was dissolved by heating it in a small quantity of methanol. After the solution had cooled and stood for some time, 0.6 g of a dark, crystalline precipitate settled out. The precipitate was dissolved in 20 ml of weak hydrochloric acid. The acid solution was clarified with activated charcoal, and ammonia was added to the clarified and filtered solution until its odor became perceptible. A brown tar was thrown down, which solidified rapidly. The solid tar was dissolved by heating it in 10 ml of 60% methanol, and the solution was hot-filtered. After the solution had cooled and stood for some time, 0.4 g of a light crystalline precipitate settled out. The precipitate was again recrystallized from 10 ml of 60% methanol, yielding 0.3 g of white crystals with a m.p. of 136-137°. The mixed melting point with the papaverinol we had synthesized by the Stuchlik method [5] exhibited no depression.

SUMMARY

1. It has been proved that papaveraldine and papaverinol are produced when papaverine is oxidized by atmospheric oxygen in the presence of activated charcoal. In view of the well-known fact that papaverinol dissolves in concentrated sulfuric acid, forming a violet solution, this fact that we have established proves that the impurity in papaverine that produces a violet color when the latter is tested with sulfuric acid is papaverinol.

2. The sensitivity of the color reaction of papaverinol with sulfuric acid has been determined.

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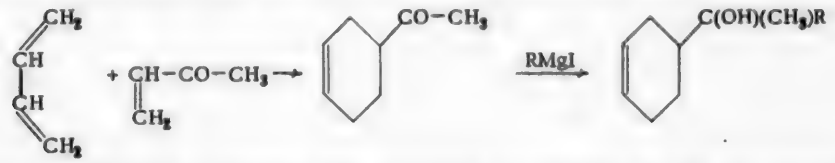
The S. Ordzhonikidze All-Union Research Institute
of Pharmaceutical Chemistry, Moscow

SOME NEW ALICYCLIC ISOMERS OF AROMATIC HYDROCARBONS

A.A.Petrov and N.P.Sopov

In one of the previous reports from our laboratory, we have described the results of our experiments on the synthesis of hydroaromatic alcohols – the isomers, homologs, and analogs of α-terpineol – from the condensation products of diene hydrocarbons with methyl vinyl ketone as follows (for divinyl) [1]:

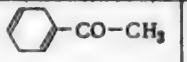
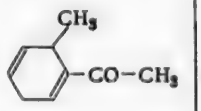
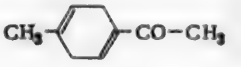


We were interested in extending these researches to the synthesis, by the same method of more highly unsaturated alcohols and in employing the latter to synthesize triene alicyclic hydrocarbons, isomers of the alkyl benzenes.

The initial substances we used in these syntheses were the condensation products of 1,3-dienes: divinyl, isoprene, and piperylene, with methyl ethynyl ketone.

The condensation product of divinyl and methyl ethynyl ketone has been described by one of the present authors [2]. The other two diene ketones have been synthesized for the first time. The constants of the diene ketones and the properties of some of their derivatives are given in Table 1.

TABLE 1

Substance	B.p. at 20 mm	d_4^{20}	n_D^{20}	Experimental	Calculated	Melting point: Semicarbazone	Melting point: Nitrophenylhydrazone
	93.5-94.5°	1.0168	1.5150	36.12	36.02	199.5-200.5	203-204
	95.5-96	0.9726	1.4985	41.08	40.64	171-172	185-186
	111-111.5	0.9872	1.5062	41.00	40.64	208-209	196-198

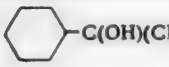
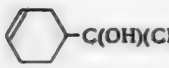
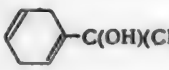
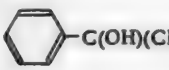
When isoprene and piperylene are condensed with methyl ethynyl ketone, we may expect two products in each condensation. Numerous experiments on the condensation of these hydrocarbons with unsaturated aldehydes, ketones, nitriles, and acids indicate that in the former case the products always have the radicals at the para position, while in the latter they are always at the ortho position [3].

The condensation of isoprene and piperylene with methyl ethynyl ketone likewise resulted in para and ortho products, respectively. This was proved by synthesizing p-cymene from the condensation product of isoprene and methyl ethynyl ketone, and of o-cymene from the condensation product of piperylene with the same ketone, as the result of the transformations described below.

The action of CH_3MgI upon the 1,4-cyclohexadiene ketones listed in Table 1 under the customary conditions yielded cyclohexadiene alcohols that are not described in the literature: dimethyl-(cyclohexadienyl)-carbinol and its homologs. Of these alcohols only dimethyl-(cyclohexadien-1,4-yl)-carbinol was isolated in the pure state. The

constants of this alcohol are compared with those of its more highly saturated and unsaturated analogs in Table 2.

TABLE 2

Substance	B.p. at 20 mm	d_4	n_D	MR_D Experimental	MR_D Calculated	References
	96°	0.9280 (at 18°)	1.472	42.92	43.09	[4]
	95.5-96	0.9479 (at 20°)	1.4824	42.20	42.62	[1]
	97.5-98	0.9788 (at 20 mm)	1.5012	41.61	42.15	–
	94 (at 13 mm)	0.9724 (at 18.5°)	1.5314	43.36	41.69	[4]

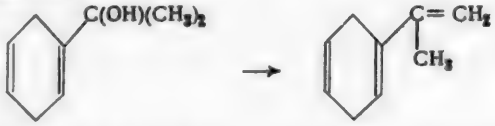
We see in Table 2 that the boiling point, the specific gravity, and the refractive index of the diene alcohol are somewhat higher than those of its more highly saturated analogs, as might have been expected. Its specific gravity is higher, though its refractive index is considerably lower, than that of dimethylphenylcarbinol.

The tertiary alcohols of the cyclohexadiene series we have synthesized are colorless liquids with a flowery fragrance.

Chemically, they are highly susceptible to dehydration, evidently because the latter results in the formation of a conjugated system of bonds.

The alcohols are dehydrated even when distilled in vacuo. This occurs so readily in the dimethyl-(methylcyclohexadienyl)-carbinols that we were unable to isolate these alcohols in the pure state. The alcohols are dehydrated very readily when distilled with a 5% solution of oxalic acid or in vacuo with an iodine crystal.

The dehydration of the cyclohexadiene alcohols ought to result in the formation of triene hydrocarbons, isomers of the aromatics, as follows:



These hydrocarbons are actually formed when dehydration is carried out by the first or second method. When iodine is employed for dehydration, the reaction products are the corresponding aromatic hydrocarbons.

No alicyclic hydrocarbons with a 1,4-cyclohexadiene ring and a vinyl group in the side ring have yet been described in the literature, it being a moot point whether they could exist or not. The references in the literature led us to think that hydrocarbons of this sort ought to be readily isomerized, possibly at the instant of their formation, into derivatives of benzene.

Of the C_nH_{2n-6} alicyclic hydrocarbons, only 1,1-dimethyl-4-methylenecyclohexadiene-2,5 and its homologs have been described in the literature at length thus far [4]. In spite of the fact that these hydrocarbons each have two radicals attached to the same ring carbon atom, they are readily isomerized by hydrochloric acid to benzene derivatives, one of the radicals shifting to the ortho position.

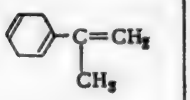
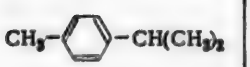
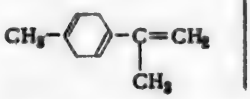
We have synthesized two vinylcyclohexadiene hydrocarbons in a fairly pure state: isopropenylcyclohexadiene-1,4 and 4-methylisopropenylcyclohexadiene-1,4. When dimethyl-(2-methylcyclohexadien-1,4-yl)-carbinol was dehydrated, the alicyclic hydrocarbon was partially dehydrated to its aromatic isomer: o-cymene. The two synthesized alicyclic hydrocarbons were colorless liquids with a rather sharp aromatic odor that differed from the odor of the corresponding aromatic hydrocarbons. Their constants are listed in Table 3.

Table 3 indicates that the vinylcyclohexadiene hydrocarbons have much higher boiling points, specific gravities, and refractive indexes than their aromatic isomers.

There is no doubt about the formulas assigned to these hydrocarbons, since the initial alcohols can be dehydrated in only one way. These formulas are borne out by all the chemical properties of the substances in question.

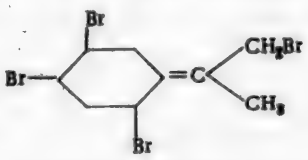
We investigated the isomerization, bromination, and oxidation of the synthesized hydrocarbons, as well as their condensation with maleic anhydride. Our experiments indicated that the vinylcyclohexadiene hydrocarbons

TABLE 3

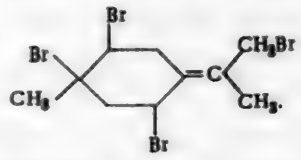
Substance	B.p.	d_4^{20}	n_D^{20}	MR_D Experimental	MR_D Calculated	References
	152-153°	0.8640	1.4947	40.54	40.16	[4]
	172-176	0.9068	1.5216	40.40	40.16	–
	177	0.8570	1.4908	45.34	44.78	[4]
	192-196	0.8903	1.5156	45.50	44.78	–

are readily isomerized to aromatic hydrocarbons by hydrogen chloride. Cumene was produced from isopropenylcyclohexadiene in this manner, as were o- and p-cymenes from o- and p-methylisopropenylcyclohexadienes, respectively. The position of the radicals in the latter substances was established by oxidation, the o-cymene yielding dimethylphthalide and the p-cymene p-[hydroxyisopropyl]-benzoic acid.

When the vinylcyclohexadiene hydrocarbons were brominated in chloroform, they readily added no more than two molecules of bromine, yielding tetrabromides. We isolated the crystalline tetrabromides of two of the hydrocarbons in the pure state. The liquid isomers are apparently produced together with the crystalline tetrabromides. The structure of the tetrabromides was not established, but it is highly probable that their formulas are as follows, on the basis of the assumption that one of the bromine molecules is added at one end of the conjugated system:



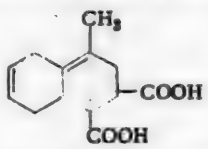
and



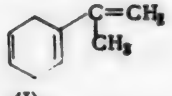
The quantity of potassium permanganate consumed when isopropenylcyclohexadiene was oxidized with an excess of a 5% permanganate solution was the equivalent of 5 gram atoms of oxygen. Acetophenone, identified as its 2,4-dinitrophenylhydrazone, was identified among the oxidation products, though no acetone was found. We were unable to isolate organic acids.

This established that oxidation of the hydrocarbon did not involve the rupture of the ring, but merely its dehydrogenation, the isopropenyl group being normally oxidized to an aceto group.

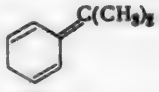
Heating the isopropenylcyclohexadiene with an equimolecular quantity of maleic anhydride yielded a crystalline condensation product, from which we secured a crystalline dibasic acid. The structure of this acid was fixed by the method of synthesis employed. It can be assigned the following formula:



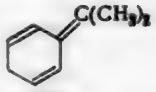
Analysis of the experimental data for isopropenylcyclohexadiene indicates that 5 out of the 6 possible formulas for the C_9H_{12} alicyclic hydrocarbon must be eliminated:



(I)

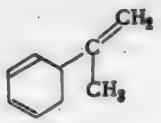


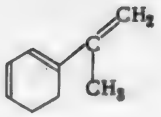
(II)

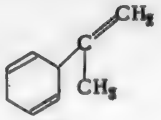


(III)

Two of them, (II) and (III), require that acetone be formed during oxidation, which is not the case. The substance with the formula (VI) does not possess conjugated double bonds and hence cannot be condensed with maleic anhydride. Thus this latter formula is likewise excluded. The substance with the formula (V) ought to exhibit a high exaltation of the molar refraction, inasmuch as it possesses a system of three conjugated double bonds. The hydrocarbon we synthesized possesses low exaltation, so that Formula (V) is not very likely. Formula (IV) must also


(IV)


(V)


(VI)

be discarded, as it is difficult to imagine that such a hydrocarbon can be formed when dimethylcyclohexadienylcarbinol is dehydrated. This isomerization would have to involve the loss of conjugation of the double bonds in the ring and the side chain. Hence, the structure of isopropenylcyclohexadiene-1,4 may be regarded as established.

EXPERIMENTAL

Synthesis of dimethyl-(cyclohexadien-1,4-yl)-carbinol. The initial ketone required for the synthesis was prepared by condensing divinyl with methyl ethynyl ketone at 110° in a toluene solution [3].

10 g of the ketone was added, with chilling and stirring, to a solution of an organomagnesium compound prepared from 3 g of magnesium and 15 g of methyl iodide in 100 ml of absolute ether. After the mixture had stood for 4 hours and been heated for 1 hour (an abundant crystalline precipitate settling out), it was poured into a flask containing a solution of ammonium chloride and pieces of ice. After the salts had been filtered out of the solution, the latter was dried with calcined Na_2SO_4, the ether was driven off, and the alcohol was distilled in vacuo. The substance decomposed violently toward the end of distillation, so that the first distillation must be run at as low a pressure as possible. We distilled the alcohol at 10 mm. It boils at 85-86° at this pressure. The constants of the alcohol are given in Table 1. The yield was 65%, based on the ketone.

Dimethyl-[cyclohexadien-1,4-yl]-carbinol is a colorless liquid with a pleasant camphor odor.

0.1719 g substance: 0.4950 g CO_2; 0.1582 g H_2O. Found %: C 78.58; H 10.30. $C_9H_{14}O$. Calculated %: C 78.21; H 10.21.

Dehydrating dimethylcyclohexadienylcarbinol. a) The slow distillation of 3 g of the alcohol at a 100-mm vacuum yielded 2.1 g of a hydrocarbon with a b.p. of 172-174° and n_D^{20} 1.5200. The hydrocarbon readily decolorized bromine water and a solution of potassium permanganate.

b) Distilling 2.6 g of the alcohol in vacuo with a small iodine crystal yielded 2.2 g of a distillate with a b.p. of 151-153° and d_4^{20} 0.8640 and n_D^{20} 1.4928, which did not decolorize bromine water or a permanganate solution. Its constants were those of cumene.

c) 2.6 g of the alcohol was distilled with a 5% solution of oxalic acid. The hydrocarbon recovered from the water [2.1 g (98%)] had the constants cited in Table 2, and its chemical properties did not differ from those of the hydrocarbon produced by the method (a).

0.1210 g substance: 0.3996 g CO_2; 0.1073 g H_2O. Found %: C 90.12; H 9.92. C_9H_{12}. Calc.%: C 89.94; H 10.06.

It should be noted that the unsaturated hydrocarbon synthesized always contained cumene as an impurity, which was readily eliminated by distillation, since there is a difference of some 20° between the boiling point of cumene and that of unsaturated hydrocarbon.

Isomerization of isopropenylcyclohexadiene. 2 g of the unsaturated hydrocarbon was heated on a water bath for 1 hour together with 2.5 ml of acetic acid and 1 ml of conc. hydrochloric acid. Then the mixture was diluted with water, and the hydrocarbon was distilled with steam. After having been washed with a NaOH solution and dried with $CaCl_2$, the hydrocarbon was distilled at ordinary pressure. B.p. 152-153°; d_4^{20} 0.8640; n_D^{20} 1.4946. The figures given in the literature for cumene have been cited earlier.

Bromination of isopropenylcyclohexadiene. A solution of bromine in chloroform was added to a solution of 0.36 g of the hydrocarbon in 5 ml of ether until no more decolorization occurred. The bromine consumed totaled 1.1 g. After the chloroform had been driven off in vacuo, the crystalline residue was transferred to a filter and washed by suction-filtering with alcohol. The 0.87 g yield of crystals with a m.p. of 110-114° thus purified constituted 60% of the theoretical. The substance was sparingly soluble in alcohol, and freely soluble in chloroform and ether. It was recrystallized by precipitating it with alcohol from a chloroform solution. The melting point of the substance thus purified was 113-114°. Colorless lamellae.

0.1182 g substance: 0.2005 g AgBr. Found %: Br 72.18. $C_9H_{12}Br_4$. Calculated %: Br 72.67.

Oxidizing isopropenylcyclohexadiene. 2.4 g of the hydrocarbon was agitated for 6 hours with a 5% solution of potassium permanganate containing magnesium sulfate. The excess permanganate was removed by adding manganese sulfate. Oxidation consumed 10.2 g of permanganate. Then the solution was distilled with steam. The upper layer of the distillate was separated, dried with $CaCl_2$, and distilled, yielding about 0.6 g of the unreacted hydrocarbon (n_D^{20} 1.5210) and a residue that proved to be acetophenone. When the residue was treated with an acetic acid solution of 2,4-dinitrophenylhydrazine, the characteristic orange dinitrophenylhydrazone settled out; it had a m.p. of 235-237°, and its mixed melting point with a known preparation of acetophenone dinitrophenylhydrazone exhibited no depression.

The crystalline precipitate of the dinitrophenylhydrazone obtained from the aqueous part of the distillate had a m.p. of 170-190° before recrystallization, whereas the acetone dinitrophenylhydrazone had a m.p. of 128°. The m.p. of the substance was 237° after recrystallization from a mixture of alcohol and ethyl acetate, the same as that of the dinitrophenylhydrazone obtained from the bulk of the substance.

The residue left in the flask was filtered out, distilled with steam, evaporated to a small volume, and acidulated with sulfuric acid. Carbon dioxide was evolved. Repeated treatment of the liquid with ether did not succeed in isolating from it any perceptible quantity of acid.

Condensing isopropenylcyclohexadiene with maleic anhydride. A solution of 0.48 g of the hydrocarbon and 0.5 g of maleic anhydride in 5 ml of toluene was heated on a boiling water bath for 5 hours, a crystalline condensation product settling out. Then the liquid was boiled with 10 ml of a 10% KOH solution, and the alkaline solution was acidulated with hydrochloric acid. An oil separated out, which crystallized when boiled with water. This yielded 0.4 g (43%) of a dibasic acid, which had a m.p. of 167-169° before recrystallization. The substance had a m.p. of 178° in a sealed capillary after it had been recrystallized from aqueous alcohol. Colorless leaflets, freely soluble in alcohol, ether, and chloroform, and sparingly so in water.

0.1928 g substance: 0.4684 g CO_2; 0.1190 g H_2O. 0.1082 g substance: 9.15 ml 0.1 N NaOH. Found %: C 66.30; H 6.91; equivalent 118.3. $C_{12}H_{16}O_4$. Calculated %: C 66.08; H 6.83; equivalent 118.1.

Synthesis of 4-methylacetylcyclohexadiene-1,4. 14.5 g of methylacetylcyclohexadiene was synthesized from 13 g of ethoxyvinylacetylene and 15 ml of isoprene (an excess) by the method previously described. The yield was 82%. The constants of the substance are given in Table 1.

0.1066 g substance: 0.3113 g CO_2; 0.0844 g H_2O. Found %: C 79.69; H 8.86. $C_9H_{12}O$. Calculated %: C 79.37; H 8.88.

The semicarbazone and the p-nitrophenylhydrazone of the ketone were prepared in the usual manner. The semicarbazone consisted of colorless leaflets, freely soluble in alcohol and sparingly in water. It was recrystallized from dilute alcohol. The p-nitrophenylhydrazone consisted of orange prisms, freely soluble in ethyl acetate, and sparingly in alcohol. It was recrystallized from a mixture of ethyl acetate and alcohol.

When isoprene was heated with methyl ethynyl ketone in toluene to 150-180°, we obtained a substance whose constants differed sharply from those of the substance described above (b.p. 109.5-110.5°; d_4^{20} 0.9889; n_D^{20} 1.52).

Synthesis of 4-methylisopropenylcyclohexadiene-1,4. Dimethyl-(4-methylcyclohexadien-1,4-yl)-carbinol was prepared from 12.2 g of the ketone described above, 2.8 g of Mg, and 17 g of methyl iodide in the usual manner. When the substance was distilled in vacuo (20 mm), all the water was split out, yielding 10.5 g of a hydrocarbon (87% yield). The constants of the substance are given in Table 2.

0.1166 g substance: 0.3832 g CO_2; 0.1135 g H_2O. Found %: C 89.68; H 10.89. $C_{10}H_{14}$. Calculated %: C 89.48; H 10.52.

Brominating methylisopropenylcyclohexadiene. A solution of 0.49 g of the hydrocarbon in 10 ml of chloroform was chilled with a freezing mixture (ice + salt), and a chloroform solution of bromine was added until no more decolorization occurred. Two molecules of bromine were used up per molecule of the hydrocarbon.

After the chloroform had been driven off in vacuo, there was left in the flask a crystalline substance that had a m.p. of 123-124° after having been washed with alcohol. The yield of washed crystals totaled 0.6 g (35%, based on the tetrabromide).

The m.p. of the substance was 126° after recrystallization by means of reprecipitation from a chloroform solution by alcohol.

0.1116 g substance: 0.1834 g AgBr. Found %: Br 69.93. $C_{10}H_{14}Br$. Calculated %: Br 70.43.

The tetrabromide was freely soluble in chloroform and ether and sparingly so in ethyl alcohol.

Isomerization of methylisopropenylcyclohexadiene. A solution of 5 g of the hydrocarbon in a mixture of 15 ml of acetic and 5 ml of conc. hydrochloric acids was refluxed on a water bath for 1 hour, after which the mixture was distilled with steam. The upper layer of the distillate was separated, washed with a soda solution, and distilled, yielding 4.2 g of p-cymene. 84% yield. B.p. 174-176°; d_4^{20} 0.8583; n_D^{20} 1.4948.

0.1326 g substance: 0.4339 g CO_2, 0.1309 g H_2O. Found %: C 89.30; H 11.05. $C_{10}H_{14}$. Calculated %: C 89.48; H 10.52.

The substance did not decolorize bromine water.

Oxidizing the substance (2.7 g) with an excess of an alkaline solution of permanganate on water bath yielded p-isopropylbenzoic acid with a m.p. of 155-157° (1.0 g), plus a small amount (0.15 g) of terephthalic acid (identified as its dimethyl ester with a m.p. of 141°). Both of these substances are characteristic products of the oxidation of p-cymene.

Synthesis of 2-methylacetylcyclohexadiene-1,4. 12.8 g of the ketone was produced from 13 g of methoxyvinylacetylene and 25 ml of piperylene (a mixture of the cis and trans forms) by the usual method. 72% yield. The constants of this substance are given in Table 1.

0.1566 g substance: 0.4536 g CO_2; 0.1192 g H_2O. Found %: C 79.04; H 8.52. $C_9H_{12}O$. Calculated %: C 79.37; H 8.88.

The semicarbazone of the ketone consisted of colorless leaflets. It was precipitated slowly. It is distinguished by its sparing solubility. It was recrystallized from dilute alcohol. The p-nitrophenylhydrazone consisted of orange crystals. It was sparingly soluble in organic solvents. It was recrystallized from a mixture of ethyl acetate and alcohol.

Synthesis of dimethyl-(2-methylcyclohexadienyl-1,4)-carbinol and its dehydration. The carbinol was synthesized from 11.4 g of the ketone, 2.6 g of magnesium, and 16 g of methyl iodide in ether. Dehydration occurred even while the ether was being driven off. Distilling the substance in vacuo (20 mm) yielded a hydrocarbon whose constants approached those of o-cymene. B.p. 72-72.5° at 20 mm, 174-178° at 755 mm; d_4^{20} 0.8828; n_D^{20} 1.5056.

0.1191 g substance: 0.3917 g CO_2, 0.1132 g H_2O. Found %: C 89.75; H 10.63. $C_{10}H_{14}$. Calculated %: C 89.48; H 10.52.

The following constants are given in the literature for o-cymene: b.p. 175°; d_4^{20} 0.876; n_D^{20} 1.5006. The slight rise in the values of the specific gravity and the refractive index over the figures given in the literature is attributable to the presence of the alicyclic isomer as an impurity.

This is also indicated by the fact that the substance decolorizes bromine water. When the substance was brominated in chloroform, about one-quarter of the bromine calculated on the basis of the hexabromide was used. We were unable to isolate a crystalline polybromide.

When 5 g of the substance was heated with hydrochloric acid in acetic acid solution, we obtained 4 g of a substance (80% yield), which did not decolorize bromine water.

The substance's constants did not differ from those cited in the literature for o-cymene.

When 2 g of the substance was oxidized by heating it on a water bath with an excess of an alkaline solution of potassium permanganate and processed in the usual manner, we secured 0.5 g of dimethylphthalide, with a m.p. of 66-68°. This substance is a characteristic product of the oxidation of o-cymene.

SUMMARY

1. Acetylcyclohexadiene-1,4 and its 2- and 4-methyl substitution derivatives have been synthesized by condensing 1,3-diene hydrocarbons: divinyl, isoprene, and piperylene with methyl ethynyl ketone. The last two substances have been described for the first time.

2. The respective hydroaromatic tertiary alcohols – diethyl-(cyclohexadien-1,4-yl)-carbinol and its homologs – have been synthesized for the first time by reacting these ketones with CH_3MgI.

3. The unexplored isomers of cumene and the cymenes – isopropenylcyclohexadiene-1,4 and 4-methylisopropenylcyclohexadiene-1,4, plus the unpurified 2-methylisopropenylcyclohexadiene-1,4 – have been synthesized by dehydrating the alcohols.

4. It has been shown that HCl readily isomerizes all these hydrocarbons to aromatic hydrocarbons – cumene and the isomeric cymenes. Brominating them yields crystalline tetrabromides.

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Leningrad Institute of Aviation Instrument Construction

substance produced had a wholly different absorption from that of both cyclohexadiene-1,3 and benzene, and that approximately 90% of the product was bromobenzene.

2) Reaction of cyclohexadiene-1,3 with quinoline hydrobromide dibromide in quinoline. 43 g of $C_9H_7N \cdot HBr \cdot Br_2$ [4,5] was chilled, and 8 g of cyclohexadiene-1,3 was cautiously added (vigorous reaction), followed by 27 g of quinoline. The contents of the flask were refluxed for about 1 hour at 110-140°, and then a fraction with a b.p. of 70-110° was distilled off. Distillation of the washed and dried product with metallic sodium yielded a fraction with a b.p. of 80-83° (2.3 g), a colorless transparent liquid that crystallized in a freezing mixture (snow and salt), whose constants agreed with those of benzene: d_4^{17} 0.8828; $n_D^{17.3}$ 1.5035; MR_D 26.12; calculated 26.31; bromine number 0.9. Ultraviolet absorption spectroscopy indicated that the product contained 90-95% of benzene.

3) Reaction of cyclohexadiene-1,3 with quinoline dibromide in quinoline. 4.1 g of cyclohexadiene-1,3 and 16 g of quinoline were added to 22 g of $C_9H_7N \cdot Br_2$ (prepared by us as a crystalline mass by adding the calculated quantity of bromine to a thoroughly chilled emulsion of quinoline in water). After refluxing for 40 minutes at 110-130°, a fraction with a b.p. of 70-95° was distilled off. After it had been washed and dried (1.8 g), it had a b.p. of 76-80° and a n_D^{16} 1.4870 (n_D^{20} 1.5017 for benzene and n_D^{20} 1.4742 for cyclohexadiene-1,3). It was found spectroscopically that the product contained about 20% of benzene.

SUMMARY

1. Ultraviolet absorption spectroscopy has been used to prove that the low-boiling fraction (b.p. 78-80.5°) of the product obtained by reacting cyclohexadiene-1,3 with quinoline tetrabromide in quinoline contains benzene, bromobenzene, and cyclohexadiene-1,3, while the high-boiling fraction (b.p. 152-158°) contains about 90% of bromobenzene.

2. The reaction of cyclohexadiene-1,3 with quinoline hydrobromide dibromide in quinoline yields a mixture of products that contains 90-95% of benzene.

3. The reaction of cyclohexadiene-1,3 with quinoline dibromide in quinoline yields a mixture of products that contains about 20% of benzene.

4. It has been shown that the second stage of the transformation of polyhalogenated derivatives of cyclohexane into aromatic compounds by heating them with quinoline involves the formation of quinoline perbromates, as indicated in the second stage of the schema suggested.

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The A.E.Favorsky Laboratory,
Leningrad State University